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THE PHYSICAL PROPERTIES OF AQUEOUS SALT SOLUTIONS IN RELATION TO THE IONIC THEORY.[1]

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IT is generally recognized that the further progress of physical science will be greatly facilitated by a better systematization of the knowledge already accumulated, and this is true in an especially high degree of the newly developed branch of science in which this section is directly interested. It has, therefore, seemed to me that the most valuable contribution that I could make toward the solution of the present problems of physical chemistry in correspondence with the aims of this Congress, would be a formulation of the present status of some of our knowledge relating to important classes of phenomena which are being actively investigated, but which have not yet received a final interpretation. It was my original hope to discuss several such classes of phenomena; but the effort involved in the collation and criticism of the available data connected with the problem which was first studied, forced me to confine my attention to that alone. This problem

[1] Address delivered at St. Louis before the Section of Physical Chemistry of the Congress of Arts and Sciences.

concerns *the physical properties of aqueous salt solutions in relation to the Ionic Theory*. This is the subject which I shall attempt to present to you: I hope that its importance and the greater definiteness that can be given to its treatment may compensate for the somewhat limited scope of this paper.

Permit me to say in advance that I have studied this subject primarily from an empirical standpoint, and that it will be my aim to present to you a series of generalized statements of the experimental results, formulated in such a way as to show their relation to the important hypotheses connected with the Ionic Theory. Unfortunately, it will not be possible in this address to reproduce, or even fully refer to, the data upon which these conclusions are based — a defect serious in a work of this kind, which will be remedied in a subsequent publication. I shall, however, try to show the general character of the evidence for each conclusion and the degree of accuracy within which it has been confirmed. I wish to add that I have been most ably assisted in the preparation of the material upon which this paper is based by Dr. J. W. Brown and Dr. M. S. Sherrill, of the Massachusetts Institute of Technology.

The principles to be first presented have reference to two of the main hypotheses which are commonly employed in quantitative applications of the Ionic Theory. One of these hypotheses is that *the migration-velocities of the ions of a salt do not vary appreciably with its concentration, at least up to a moderate concentration; and consequently, that the degree of ionization is equal to the ratio of the equivalent conductivity at the concentration in question to the limiting value of the equivalent conductivity at zero concentration* — a ratio which I will hereafter call simply the conductivity-ratio. The other hypothesis is that *ions, and also the un-ionized molecules accompanying them, produce an osmotic pressure substantially equal to the pressure exerted by the same number of gaseous molecules at the same temperature, at least up to a moderate concentration;* a hypothesis which may be more briefly expressed by the statement that the osmotic pressure-constant for dissolved electrolytes is identical with the gas-constant. It is evident that with the help of this hypothesis we can calculate, either from measurements of osmotic pressure or from those of any other property which is thermodynamically related to osmotic pressure, the number of mols in the solution resulting from one formula weight of salt, that is, the quantity which van't Hoff has represented by the letter *i*. From

the latter, provided the ionization is not complicated by the formation of complex molecules or ions, the degree of ionization is readily derived.

The first of these hypotheses cannot be independently tested, because no direct method of determining the change of migration-velocity with the concentration, is known. But the following principle, which has an important significance with reference to the *relative* influence of concentration on the velocities of different ions, has been established by measurements of the concentration-changes at the electrodes attending the electrolysis of salt solutions.

The transference number, or ratio of the conductivity of one ion to the sum of the conductivities of both ions, is constant within one per cent., between the concentrations of $\frac{1}{200}$ *and* $\frac{1}{10}$ *normal, for all salts thus far accurately investigated, except lithium chloride, the halides of bivalent metals, and cadmium sulphate.*

This principle holds true, according to the results of various investigators, in the case of potassium and sodium chlorides, hydrochloric and nitric acids, silver nitrate, barium nitrate, potassium sulphate, and copper sulphate — thus in the case of salts of the three different ionic types, which I will speak of as the uni-univalent, the unibivalent, and the bi-bivalent types, in correspondence with the valences of the two ions composing the salt.

Two conclusions are to be drawn from this result. The first is, that complex ions are not present in important quantity in the solutions of these salts. And the second is, that the migration-velocities of the two ions of a salt vary by the same percentage amount, if they vary at all, with changes in its concentration. It is scarcely admissible, however, to regard this last fact even as an indication that the hypothesis of constant migration-velocities is correct; for any change in the character of the liquid medium might well affect the velocities of different ions not far from equally.

Important evidence in regard to this hypothesis and that stating that ions and the un-ionized molecules associated with them have a normal osmotic pressure is, however, furnished by the agreement of the ionization values derived, on the one hand, from the conductivity-ratio, and, on the other, from the properties thermodynamically related to osmotic pressure. Three of these properties have been measured with sufficient accuracy with certain electrolytes to make the results of significance, namely, the freezing-point lowering, the electromotive force of concentration cells, and the heat of solution in relation to

change of solubility with the temperature. Under the assumption that osmotic pressure and gaseous pressure are equal under identical conditions, a relation between each of these properties and the degree of ionization of an electrolyte can be derived with the help of the second law of energetics. Then, either this ionization value may be directly compared with the conductivity-ratio, or, assuming provisionally that the latter is a correct measure of ionization, the magnitude of the property in question may be calculated, and the result compared with that obtained by direct measurement. In the case of the freezing-point lowering, I have adopted the first of these methods. For the five salts for which both reliable freezing-point determinations and accurate conductivity measurements at 0° exist, the ionization values corresponding to both of these properties have been computed. Especial attention was given to the selection of the best value of the freezing-point lowering constant and to the extrapolation of the conductivity for zero concentration, the details of which cannot be here described. The results may be summarized as follows:

In case of the two uni-univalent salts and the three unibivalent salts hitherto carefully investigated, the ionization values derived from freezing-point lowering do not differ from those derived from conductivity, between the concentrations of $\frac{1}{200}$ *and* $\frac{1}{4}$ *normal, by more than 2 or 3 per cent.*

The five salts referred to are potassium and sodium chlorides, potassium and sodium sulphates, and barium chloride. The two sets of values for potassium chloride, for which an abundant experimental material exists, exhibit no pronounced or systematic differences; but for the other four salts the freezing-point leads to values which are in general from two to three per cent. higher at all concentrations than the conductivity-ratio. The fact that these differences do not, as a rule, increase with increasing concentration indicates that they may be due to some constant experimental error, or to an error in the extrapolated conductivity value.

Accurate measurements have been made by Jahn of the electromotive force of concentration cells consisting of two silver or mercury electrodes covered with silver chloride or mercurous chloride, one of which is immersed in a weak solution and the other in a strong solution of sodium or potassium chloride. These measured values were compared by him with those calculated from the thermodynamic relation between electromotive force and the concentrations and degrees

of ionization of the salt in the cell. Unfortunately, however, the thermodynamic relation employed involved the assumption that the ionization varies with the concentration in accordance with the Mass-Action Law — an assumption which is known not to be true of the ionization values derived from conductivity. The assumption is, therefore, an irrational one — one by which the question at issue is prejudged. What should be done in calculating the electromotive force so as to determine whether the conductivity ratio gives ionization values consistent with the measured electromotive forces, is evidently to assume that the ionization changes with the concentration in the way that the conductivity indicates that it does. Arrhenius recognized this error and partially corrected for it by a method of approximation. I have repeated the calculations by an exact thermodynamic formula based on an empirical law expressing the change of the conductivity-ratio with the concentration, to which I will refer later. The results are summed up in the statement that, *when the conductivity-ratio is assumed to represent the degree of ionization of the salt, the calculated values of the electromotive force of concentration cells exceed the measured ones by only about one per cent. in the case of potassium and sodium chloride between the concentrations of* $\frac{1}{600}$ *and* $\frac{1}{200}$ *normal.* The measured electromotive force corresponds to an ionization value at the latter concentration about one per cent. less than the conductivity-ratio.

The thermodynamic relation involving heat of solution has been accurately tested with only one salt — potassium perchlorate; but since it is a different salt from those used in the other experiments, and since its concentration was fairly high — $\frac{1}{8}$ normal — the result is of interest. It was found that the *measured heat of solution was less by only 1.1 per cent. than that calculated under the assumption that the conductivity-ratio is equal to the degree of ionization.* The measured heat of solution corresponds to an ionization value $2\frac{1}{2}$ per cent. lower than the conductivity-ratio.

With respect to these small deviations of the results obtained by the three methods of comparison, it is important to note that they lie in opposite directions, the freezing-point lowering corresponding to larger values of the ionization, and the measured electromotive forces and heat of solution to smaller ones than the conductivity-ratio. This fact makes it almost certain that they are due to experimental errors. Nevertheless, further exact measurements of all these properties are highly desirable.

From a theoretical standpoint these three methods are based on the same hypotheses — namely, that the osmotic pressure-constant for ions and un-ionized molecules is identical with the gas-constant; that the conductivity-ratio is a correct measure of ionization, and that complex molecules or ions are not present in the solution. The concordance of the results furnishes, therefore, a strong confirmation of the correctness of these fundamental hypotheses. The only alternative conclusion is that an error in one of these hypotheses is compensated by an error of opposite effect in one of the others; but it seems very improbable that such a compensation could occur in the case of so many salts of different chemical nature and different types through the range of concentration ($\frac{1}{200}$ to $\frac{1}{4}$ normal) for which the agreement of the experimental results has been shown to hold true. It is certainly more consistent with the modern methods of science to adopt these simpler hypotheses, which are in full accord with the considerable number of facts thus far known, than deliberately to introduce more complicated assumptions for which there is at present no experimental warrant.

The combination of these hypotheses with the experimental values of the quantities involved at varying concentrations makes necessary the further conclusion that the *degree of ionization of salts, whether derived from the conductivity-ratio or from thermodynamic relations involving the equality of the osmotic-pressure-constant and the gas-constant, does not vary with the concentration even approximately in accordance with the Law of Chemical Mass-Action.*

This empirical consequence of the fundamental hypotheses of the Ionic Theory has led several investigators to raise a theoretical objection to them, it being contended that the laws of thermodynamics require that the validity of these hypotheses involves that of the Mass-Action Law itself. This apparent inconsistency between the inductive and deductive conclusions makes it probable that some unproved, erroneous assumption is tacitly involved in the theoretical derivation. That there is, in fact, a possible alternative, which has, I believe, been previously overlooked in the thermodynamic discussions, will be evident from the following considerations. The thermodynamic relations between ionization and freezing-point, electromotive force, or heat of solution, involve only the assumption that the work done in reversibly separating water from a solution at constant concentration is equal to that done in producing the same volume-change in a gas, which implies, of course, that the ions and un-ionized molecules have in the presence

of each other normal osmotic pressures. On the other hand, the derivation of the Mass-Action Law equation is based on cyclical processes, which necessarily involve the separate introduction and removal of the un-ionized molecules and of the ions into or from solutions of different concentrations, and it further involves the assumption that this introduction or removal of molecules or ions can be effected by the application of an external pressure equal to that osmotic pressure which each of them possesses in the mixture; that is, the possibility is ignored that the separation of the molecules from the ions may itself give rise to some new force, and may involve, consequently, another quantity of work than that corresponding to the osmotic pressure. The Ionic Theory would evidently predict a result of this kind if an attempt were made to separate the positive ions from the negative, even though their osmotic pressures when present together were perfectly normal; and it is quite conceivable, even though the reason for it be not apparent, that the separation of the un-ionized molecules from the ions, with which they may be in electrical as well as chemical equilibrium, should involve an abnormal quantity of work. The assertion that the validity of the osmotic pressure principle necessarily implies that of the Mass-Action Law is therefore unwarranted from a deductive standpoint; while the inductive evidence, pointing strongly as it does to the substantial correctness of the former principle and the complete inadequacy of the latter one, makes it highly probable that the *separation of un-ionized molecules from ions does involve the expenditure of other work than that corresponding to their osmotic pressures.*

Since the ionization does not change with the concentration in accordance with the Mass-Action Law it is natural to inquire what the law of its change is. This matter has been investigated from an empirical standpoint by several investigators with the help of the conductivity data. The results justify the statement of the following principles:

The un-ionized fraction of a salt as determined from the conductivity-ratio is proportional to the cube-root of its total concentration, or to that of its ion-concentration, between $\frac{1}{2000}$ *and* $\frac{1}{10}$ *normal, in the case of both uni-univalent and unimultivalent salts.* That is, $1 - \gamma = Kc^{\frac{1}{3}}$, or $1 - \gamma = K(c\gamma)^{\frac{1}{3}}$, where γ is the degree of ionization, c the concentration, and K a constant. The first of these functions was proposed by Kohlrausch, the second by Barmwater. Owing to the relatively small variation of the ionization, these two functions cannot differ much as

to their constancy, but on the whole the experimental data indicate that the second function is somewhat more constant. The average deviations of the actual measurements from the values corresponding to this function are $\frac{1}{4}$ per cent. in the case of ten uni-univalent salts, $\frac{1}{3}$ per cent. in the case of nine unibivalent salts, and also $\frac{1}{3}$ per cent. in the case of three uni-tri- and uniquadrivalent salts. The maximum deviations are two or three times as great. It is of interest to note that the strong mineral acids, hydrochloric and nitric, behave like salts in this respect. These functions have been shown to apply to potassium and sodium chlorides through a range of temperature extending from 18° to 306°. They do not apply at all closely to such salts of the bi-bivalent type as magnesium and copper sulphates, perhaps owing to appreciable hydrolysis. Nor do they represent satisfactorily the experimental data for any kind of salts at the very low concentrations lying between $\frac{1}{100000}$ and $\frac{1}{2000}$ normal, nor at concentrations higher than $\frac{1}{5}$ normal.

The experimental results are also well expressed by the statement that *in the case both of uni-univalent and unibivalent salts, between the concentrations of* $\frac{1}{10000}$ *and* $\frac{1}{5}$ *normal, the concentration of the un-ionized molecules is proportional to the concentration of the ions raised to a constant power, varying somewhat with the salt and the temperature, but as a rule only between the limits of 1.43 and 1.56.* That is, $c(1-\gamma) = K(c\gamma)^n$, where $n > 1.43$ and < 1.56.

This general function was first applied by Storch and was afterwards further discussed by Euler and Bancroft. It has the advantage over the previous ones that it represents the data with accuracy even up to the highest dilutions, and therefore can be used for obtaining the limiting conductivity at zero concentration.

The applicability to the salts of different types of either of these principles governing the change of ionization with the concentration leads to the important conclusion that *the form of the concentration function is independent of the number of ions into which the molecules of the salt dissociate.* This remarkable fact, though previously recognized, has not been sufficiently emphasized, and it has been often ignored in discussions of the cause of the deviation of the ionization of salts from the requirements of the Mass-Action Law. It seems to me to show almost conclusively that chemical mass-action has no appreciable influence in determining the equilibrium between ions and un-ionized molecules. How complete the contradiction with the Mass-

Action Law is, may be illustrated by citing the specific facts that for di-ionic, tri-ionic, and tetra-ionic salts this law requires that the concentration of the un-ionized molecules be proportional to the square, the cube, and the fourth power, respectively, of the concentration of the ions; while the experimental data show that it is approximately proportional to the $\frac{3}{2}$ power of that concentration, whatever may be the type of salt.

Having seen in what manner the degree of ionization varies when the concentrations of both ions of the salt are simultaneously varied by dilution, it is of interest to determine the effect of changing the concentration of either ion separately. A study of the conductivity and the freezing-point of mixtures of two salts having one ion in common throws much light upon this question, for the following simple principle has been found to represent this phenomenon: *The conductivity and the freezing-point lowering of a mixture of salts having one ion in common are those calculated under the assumption that the degree of ionization of each salt is that which it would have if present alone at such an equivalent concentration that the concentration of either of its ions were equal to the sum of the equivalent concentrations of all the positive or negative ions present in the mixture.*

This somewhat complicated statement may be illustrated by the following example: Suppose that a mixed solution is 0.1 normal with respect to sodium chloride and 0.2 normal with respect to sodium sulphate, and that it is 0.18 normal with reference to the positive or negative ions of these salts. The principle then requires that the ionization of either of these salts in the mixture be the same as it is in water alone when its ion-concentration is 0.18 normal.

This principle in regard to the conductivity of mixtures, which has been definitely stated by Arrhenius, is shown by the existing data to hold true almost, if not quite, within the small experimental error of the determinations both for mixtures of salts of the same type and for those of salts of different types up to a concentration of at least $\frac{1}{2}$ normal. Experiments confirming this principle have been made upon eight pairs of uni-univalent salts by Arrhenius, Manson, and Barmwater. In addition, the principle has been shown by several Canadian investigators, Archibald, McKay, and Barnes, to hold true for mixtures of potassium and sodium sulphates, potassium and copper or magnesium sulphates (up to 0.1 normal), potassium sulphate and chloride, barium and sodium chlorides, and zinc and copper sulphates — thus for almost

every possible typical combination of uni-uni-, uni-bi-, and bi-bivalent salts. That the same principle is true of the freezing-point lowering is shown by the measurements of Archibald with mixtures of potassium and sodium sulphate. This proves that the phenomenon really has reference to the degree of ionization and that it does not arise from a possible variation in the migration-velocities of the ions.

Of especial interest is the relation of this principle to the validity of the Mass-Action Law. Almost all investigators of the conductivity of mixtures have concluded from the fact that upon mixing solutions of equal ion-concentration there is no change in ionization, that the results do conform to this law. Yet it is scarcely conceivable that this law can apply to mixtures of salts in which the concentration of one ion is varied while maintaining that of the other constant, in view of the fact that it is known not to hold true for the variations of the concentrations of both ions produced by dilution. And in reality this conclusion, if regarded as a general expression of the facts, is entirely unwarranted. It is true that for certain typical combinations of salts — those for which from one molecule of each salt results by ionization not more than one ion of the kind not common to the salts — the principle here stated does coincide with the requirement of the Mass-Action Law. But for combinations not so characterized the Mass-Action Law predicts, as is readily seen upon formulating the equations, a conductivity of the mixture widely divergent from that actually found, and, therefore, from that expressed by the principle under consideration. This last statement applies, for example, to the mixtures before referred to of potassium sulphate with sodium sulphate, and of potassium sulphate with copper or magnesium sulphate, the first of which have been studied both with respect to their conductivity and freezing-point. The Law of Chemical Mass-Action here again shows itself entirely inapplicable to the phenomena connected with the ionization of salts. That some investigators have thought that the deviations from this law indicated by the conductivity were only apparent, and that they were attributable to variations in the migration-velocity, has arisen, no doubt, from the fact that they have confined their attention to di-ionic salts, and have failed to recognize, on the one hand, the striking divergences from it exhibited by tri-ionic salts, and, on the other, the substantial correspondence of the conductivity and freezing-point results.

Combining this principle in regard to the ionization of mixed salts in solution with the empirical concentration law of Storch for single

salts, we are led to the conclusion that the ratio of the concentration of the un-ionized part to the product of the concentrations of the two ions (but in the case of tri-ionic salts *not* raised to a power corresponding to the requirements of the Mass-Action Law) is a function of the sum of the equivalent concentrations of all the ions in the solution and of that alone.[1] This ratio is, moreover, roughly inversely proportional to the square root of the total ion-concentration.

The correctness of this principle is further demonstrated by the fact that with its aid the conductivity of a mixture of two salts without a common ion can be computed from their separate conductivities. This is shown by the conductivity measurements, made by Archibald and more recently by Sherrill, upon mixtures of potassium chloride and sodium sulphate, or of sodium chloride and potassium sulphate. Up to at least 0.2 normal concentration, the agreement between the observed and calculated values is within 0.5 per cent. On the other hand, the divergence of the observed values from the requirement of the Mass-Action Law amounts to many per cent.

It seems appropriate at once to supplement these principles in regard to the form of the concentration function by a statement of two general rules which have been found to express the magnitude of the ionization of salts of different types. These rules, unlike the preceding principles, are only crude approximations; but, nevertheless, they prove of some assistance in rough applications of the Ionic Theory, and undoubtedly possess an important theoretical significance not yet recognized. They may be stated as follows: (1) *the decrease of ionization with increasing concentration is roughly constant in the case of different salts of the same type;* and (2) *the un-ionized fraction at any definite molal concentration is roughly proportional to the product of the valences of the two ions in the case of salts of different types.* Thus, at 0.1 normal concentration the mean value of the degree of ionization for 17 uni-univalent salts measured at 18° is 83.3 per cent., the average deviation of the separate values from this mean is 2.1 per cent., and the maximum deviation of any of them is 5.4 per cent. of the mean value; while for fourteen unibivalent salts the mean value is 69.8 per cent., the average deviation 5 per cent. of this, and

[1] This is expressed mathematically by the following equation, in which c_1 and c_2 represent the equivalent concentrations of the two salts, and γ_1 and γ_2 their degrees of ionization in the presence of each other: $\frac{c_1\gamma_1(c_1\gamma_1 + c_2\gamma_2)}{c_1(1-\gamma_1)} = K_1(c_1\gamma_1 + c_2\gamma_2)^{n-1}$.

the maximum deviation about 10 per cent. of it. The un-ionized fraction in $\frac{1}{20}$ molal solution is $13\frac{1}{2}$ per cent. for these univalent salts; 30 per cent., or about twice as great, for the unibivalent salts; and 60 per cent., or about four times as great, for the three bi-bivalent salts investigated (zinc, magnesium, and copper sulphates). The salts of mercury and cadmium are pronounced exceptions to the rule.

Far more extensive material for testing these rules is furnished by the measurements made at 25° between the concentrations of $\frac{1}{32}$ and $\frac{1}{1024}$ normal. In the case of the uni-univalent salts, data exist at this temperature and these concentrations for thirty-six inorganic salts, about sixty-five sodium salts of organic acids, and about an equal number of hydrochlorates of organic bases. A consideration of all these data shows that, with only three or four exceptions not of a pronounced character, the values of the degree of ionization of all these salts in $\frac{1}{32}$ normal solution lie between the limits of 84 and 90 per cent. and are fairly uniformly distributed throughout this range of 6 per cent. For sixty-seven unibivalent salts the corresponding limits of the ionization values are 72 and 81 per cent., while for only four such salts do the values lie beyond these limits. For the six unitrivalent salts investigated the range is from 67 to 76 per cent.; for the three uniquadrivalent salts from 59 to 63 per cent.; and for twelve bi-bivalent salts from 49 to 63 per cent., while three such salts show more considerable variations. The values of the un-ionized fraction corresponding to the mean of these two limits for the different types of salts at the same equivalent concentration increase somewhat more slowly than the product of the valences of the ions. The proportionality becomes a fairly close one, however, when the salts are compared at the same molal instead of the same equivalent concentration. Thus, with the help of the Kohlrausch concentration-function, it is calculated from the preceding values that the un-ionized fractions in $\frac{1}{32}$ molal solution are as follows:

13 per cent. for the uni-univalent salts,
$29\frac{1}{2}$ per cent. for the unibivalent salts,
41 per cent. for the unitrivalent salts,
62 per cent. for the uniquadrivalent salts,
55 per cent. for the bi-bivalent salts,

which are seen to be approximately the required multiples of the constant factor 14.

Before leaving this subject it should be stated that the results

conform, on the whole, about equally well with the rule that *the decrease of equivalent conductivity* (*instead of ionization*) *is roughly constant for salts of the same type;* and, when the comparison is made at the same equivalent concentration, distinctly better to the rule that the *decrease of equivalent conductivity is proportional to the product of the valences of the ions for salts of different types.* When compared at the same *molal* concentration, however, this rule does not apply. These rules were originally stated by Ostwald. They differ not inconsiderably from those expressing the change in ionization — namely, to an extent corresponding to the variations of the conductivities at extreme dilution. The deviations are so irregular, however, that, from an empirical standpoint, the choice between the two pairs of rules is arbitrary. In either form these rules seem to justify the inference that the degree of ionization of salts, unlike that of the organic acids and bases, is not primarily a specific chemical property determined by chemical affinity, but that it is determined, at least in the main, by the magnitude of the electric charges on the ions.

The establishment of the principle in regard to the ionization of a mixture of salts has a direct bearing on the phenomenon of the effect of one salt on the solubility of another with a common ion. It has been usually assumed that in a (not too concentrated) saturated solution the un-ionized molecules of the salt always have the same concentration; and, secondly, that the product of the *ion* concentrations (each raised to a power corresponding to the number resulting from one molecule) also retains the same value. And the experimental results in several cases have been shown to accord fairly well with these two hypotheses. Yet their simultaneous validity is quite inconsistent with the principle in regard to the ionization in mixtures. In fact, when considered in the light of this principle, the existing data lead to the conclusion that the former hypothesis is not even approximately true, and that the latter one, at any rate in cases where the ionization is far from complete, is affected by a considerable error. One example may be cited: when thallium chloride and bromate, each of which alone has a solubility of about $\frac{1}{40}$ normal in water at 40°, are simultaneously present as solid phases, the solubility of each is reduced by the other to an extent which shows that the concentration of the un-ionized molecules is diminished by about 15 per cent. and that the product of the ion-concentrations is increased by about 5 per

cent. This case is a typical one; but what the quantitative law of the influence in question is, can be determined only by a further study of the phenomenon. In the case of tri-ionic salts, the ion-concentration product is even approximately constant, only when the square — not when the first power — of the concentration of the univalent ion is employed. This has been shown by experiments with lead iodide in the presence of potassium iodide, with lead chloride in that of other chlorides, and with calcium hydroxide in that of ammonium chloride.

I will close by calling your attention to a remarkable principle in regard to the properties of salt solutions, of a character quite distinct from those thus far considered. That many properties of dilute salt solutions can be expressed as the sum of values assigned once for all to the constituent radicals or ions was long ago recognized, and has often been cited as a corollary from the Ionic Theory. That this additivity of properties persists up to fairly high concentrations is a fact, however, that has received scant consideration, owing to its apparent lack of relationship to that theory. This fact is shown strikingly in the case of certain highly specific optical properties which are ordinarily found to be dependent in a high degree on molecular structure. Thus, the experimental data fully warrant the statement of the principle that *the optical activity and the color of salts in solution, when referred to equivalent quantities, are independent of the concentration and therefore of the degree of ionization of the salts, and are additive with respect to the properties of the constituent ions even up to concentrations where a large proportion of the salt is in the un-ionized state.* Abundant data might be cited in support of this principle, especially with reference to optical activity. But I can only illustrate the character of the evidence by presenting a few of the results obtained by Walden with the salts of α-brom camphor sulphonic acid. In $\frac{1}{30}$ normal solution he found the following values of the molal rotatory power:

Lithium salt . . .	275	Acid itself . . .	273
Sodium salt . . .	272	Beryllium salt . . .	274
Potassium salt . . .	273	Zinc salt . . .	272
Thallium salt . . .	273	Barium salt . . .	272

The values are seen to be substantially identical, although the conductivity shows the acid to have an un-ionized fraction of 7 per cent., the salts of the univalent metals one of 16 per cent., and those of the bivalent metals one of 30 per cent., and although the un-ionized

molecules present contain in some cases the elements hydrogen, lithium, and beryllium of very small atomic weights, and in two others the elements thallium and barium of large atomic weights.

If there were not other evidence to the contrary, the existence of this general principle, which is also applicable to many other properties, would almost warrant the conclusion that the salts are completely ionized up to the concentration in question, and that the decrease in conductivity is due merely to a change in migration-velocity. But, in view of the apparently conclusive evidence against such a hypothesis, we can only conclude that the form of union represented by the un-ionized molecules of salts differs essentially from ordinary chemical combination, it being so much less intimate that the ions still exhibit their characteristic properties, in so far as these are not dependent upon their existence as separate aggregates.

These, then, are the empirical principles to which a critical analysis of the experimental data leads. Upon these principles must be based the rational, theoretical explanation of the phenomena in question. The discovery of that explanation constitutes one of the most important of the present problems of physical chemistry.

SANITARY PLUMBING AND OUR PLUMBING LAWS, WITH SUGGESTIONS FOR THEIR REVISION AND SIMPLIFICATION.

By J. PICKERING PUTNAM.

(Read November 10, 1904.)

It is now recognized by students of the subject that both legislation and common practice in one of the most important lines of sanitary engineering have for a long time been directly opposed to the actual demonstrations of science, and to the teachings of acknowledged authorities.

The public has preferred to submit to a very burdensome form of taxation rather than, by independent experiment on suitable apparatus, to establish the truth for itself by proper proofs where conflicting opinions as to the facts exist. It has assumed the right to legislate, but not always to investigate, and this even in cases where direct investigation is clearly essential to serviceable legislation.

Since, however, no attempt at exhaustive public investigation had been made, so far as I could ascertain, to establish a sound basis for plumbing legislation, and since the public records of private investigations were both incomplete and fundamentally conflicting, I decided so far back as 1883 to make an attempt myself to obtain sufficient data for independent judgment by careful original experiment, and the work has been carried on up to the present time. These investigations were made originally in behalf of a medical client who, like myself, considered sanitation of primary importance in the construction of his house. They have established certain facts which had previously been in dispute, and have suggested certain improvements of a fundamental character, which will be placed before you tonight.

The committee on the revision of the building laws, appointed this year by the Boston Society of Architects, have invited their fellow-architects to aid them by sending suggestions for such revision to be presented to the legislature this winter, and this invitation is responsi-

ble for the demonstrations and suggestions you are to consider with us tonight. It is with the hope of being able to aid our legislators in preparing for us a simpler and better code of plumbing laws that this

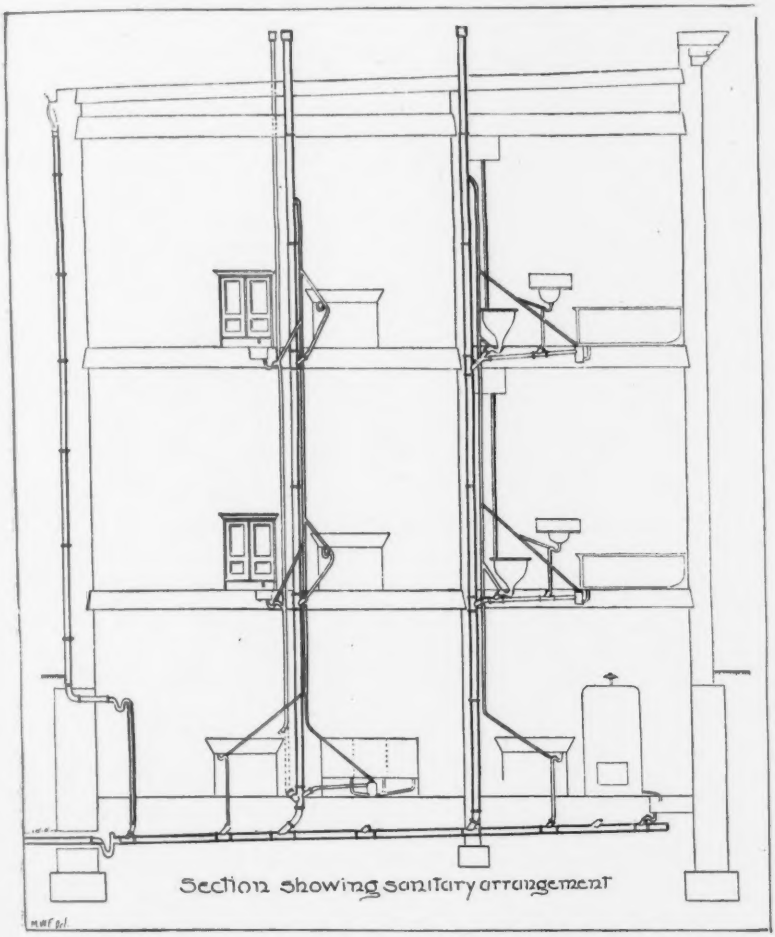

FIG. 1. — SYSTEM OF PLUMBING REQUIRED BY THE BUILDING LAWS OF BOSTON.

apparatus has been constructed, and it is for this that the distinguished gentlemen whose names you have seen on the tickets have been invited to aid in the discussion.

I have before me the plumbing ordinances of Boston, which are

substantially in accord with those of the majority of large cities throughout the country, and I have submitted amendments to a number of the most important provisions in these laws. All of these amendments are in the direction of simplification.

Our first illustration, Figure 1, presents the system of plumbing required by the Boston Building Laws, the cut having been reduced from the plate printed in the Statutes issued by the Building Department. After this I shall show you a simpler system, embodying most of the amendments now advocated by the best authorities.

Let us first enumerate briefly these amendments in the order of their importance, and afterwards explain the reasons for each in detail.

Back Venting. — More than half of the increased complication is due to the so-called "back venting" of the traps of all the fixtures. Here, for instance (Figure 1), are bath tubs, wash basins, and other fixtures, whose traps consist in bends in the pipe deep enough to present a barrier to the passage of air from the drain pipe into the house. Our building law requires every such trap to be vented by a special air pipe extending from the sewer side of the trap up to a point above the highest fixture on the stack, as shown on our diagram, by the smaller pipe between the fixtures and the 4-inch soil pipe.

The original purpose of the law was to protect the trap seals from what is called "siphonage." But soon after it was enacted, the discovery was made that the air current induced by the back-vent pipe was itself far more mischievous than the danger it was expected to remove, in that it operated to destroy the seal by evaporation; and so rapidly did it do this in some cases that, in at least one large city, the Board of Health felt obliged to issue notices to house owners, advising them to have the traps refilled by hand in houses temporarily unoccupied, as often as once a fortnight, in order to restore the seal destroyed by back venting.

It was also very soon found that the system was unreliable, on account of deposits of greasy sediment within the vent pipe and of snow or frost at its top, which rendered it inoperative.

Other difficulties and dangers revealed themselves as time went on, as I shall show directly.

On the other hand, methods of securing positive protection without back venting were multiplied, until today the thinking man is puzzled to understand how the public can continue to allow such a foolish and costly method of ***ensuring insecurity*** to exist.

Main House Trap. — The next important modification of the law recommended consists in the omission of the main house trap shown in the basement (Figure 1), and of the external sewer vent (Figure 15) often necessitated by its use.

Fixture Outlets. — A third modification consists in requiring every fixture to be constructed with an outlet large enough to fill its waste pipe "full bore," in order to keep these pipes clean by thorough flushing.

Fewer Traps. — A fourth consists in reducing the number of fixture traps required. The law now calls for a separate trap under each fixture, no matter how near to one another they come. An exception is made, however, in the case of several adjoining wash trays, which are allowed to have a single trap between them. This good feature should be extended to all adjoining fixtures. I hope to be able to show you that it is much more scientific, as well as much safer and more economical, to use one trap in such cases than several.

Traps at Level of Floor. — Moreover, it is, for important reasons, better to place the trap at or below the floor level than close to the fixture it serves, as is now required by law.

Rain-water Trap. — A sixth modification consists in omitting in most cases the trap now called for on all rain-water leaders, because a trap here reduces the ventilation, and increases the complication and expense. But more than this, the trap prevents the use of the main soil pipe as a rain-water conductor. There is no possible way of flushing the soil pipe better than by admitting rain water where the combined system of sewerage is used.

Lead-calked Joints. — A seventh modification consists in striking out the restriction in the law limiting the jointing of cast-iron pipes to lead calking. Probably no more unscientific method of construction now exists in the whole domain of house building than this, iron and lead having no more constructive affinity for each other in jointing than cats and dogs. Other really scientific methods of jointing cast iron have recently come into the market which are both reliable and much cheaper.

Cistern Supply. — Finally, the provision requiring water-closets to be supplied from cisterns with flush pipes not less than an inch in diameter should be modified. Better and simpler means for flushing are now known.

Omission of Trap Vent. — Let us now examine more in detail our first proposed modification relating to the trap-vent law, and, in order fully to understand this, we must have a very clear idea of the phenomena of "siphonage" and "back pressure."

Figure 2 gives a very clear idea of these mischievous forces. The main soil pipe is shown in the centre, and the back-vent pipe at the left. It is taken from the actual plumbing work used in a four-story office building in Boston, upon which I made my first experiments in 1884 for the Board of Health.

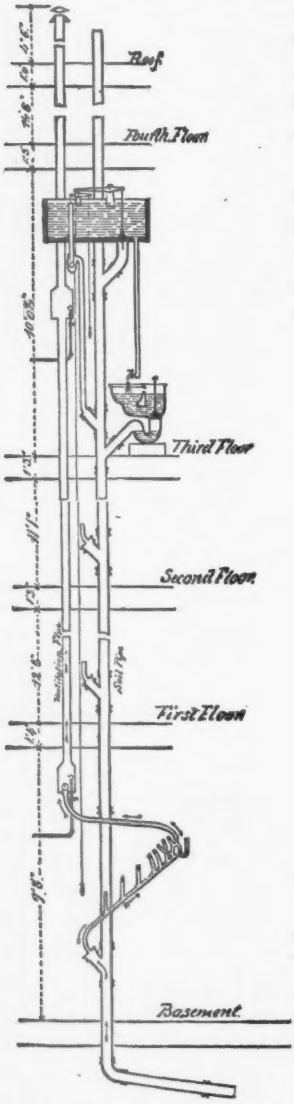

FIG. 2. — APPARATUS FOR EXPERIMENTS MADE IN 1884 FOR THE BOSTON BOARD OF HEALTH.

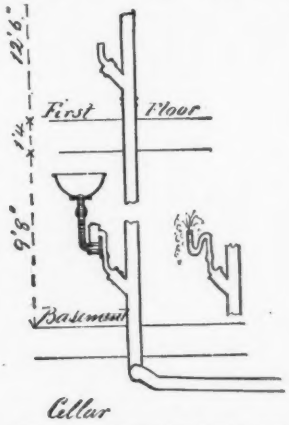

FIG. 2a. — PART OF APPARATUS REPRESENTED IN FIGURE 2 MODIFIED TO SHOW BACK PRESSURE.

When water is discharged from the tank in the third story it descends through the soil pipe in the form of a plug, or piston, and rarifies the air behind it, because the friction of the walls of the pipe prevents the air from the top of the pipe from following the water as fast as it falls. Consequently the water seal of a trap placed

on either of the branches below the tank will suffer by siphonage, because of the reduction of the atmospheric pressure upon the inner end of the seal. In other words, the inertia of the water in the trap affords less resistance to the air than the friction along the sides of the soil pipe, and if the trap is improperly constructed its water seal is forced out in advance of the inrushing air current, and this action is called "siphonage."

Back pressure is the reverse of siphonage. As the plug of water discharged from the tank descends toward the sharp bend shown in the basement (Figure 2*a*), the air in front of the falling plug is compressed, because the sharp bend retards its escape, and this compressed air seeks a passage at every outlet. Back pressure is, therefore, evidently strongest at branches which are near the bend in the basement, and siphonage is strongest at branches which are farthest from this bend. We have at the end of the basement branch (Figure 2) an ordinary so-called S-trap. This trap possesses in itself almost no power of resistance to siphonage.

Figure 7 represents an apparatus for demonstrating the siphonage of traps under various conditions. I have produced by means of this pump a partial vacuum in this large pipe (Figure 7), which represents our soil pipe. If now we allow air to pass through this small S-trap by opening the stopcock between it and the soil pipe, you see that the air has actually forced out enough of the water to entirely destroy the seal, leaving a free passage for soil-pipe air, sometimes called "sewer gas," to enter directly into the house.

Even the seal of this large trap on the left of the apparatus is destroyed in precisely the same manner. The trap is now full of water up to its overflow. If we connect it with the partial vacuum in the soil pipe by opening this large stopcock, the atmospheric pressure will break its seal very rapidly and forcibly, as you see. I have produced here a greater degree of vacuum than occurs in practice for the purpose of presenting the phenomenon to you more strikingly. The apparatus being built for comparative as well as positive tests, it is capable of illustrating any degree of partial vacuum desired. Later we will consider the degree encountered in actual plumbing practice.

Now the back-vent pipe shown in Figures 1 and 2 was invented with the idea of providing an inlet for the air on the soil-pipe side of the trap, so that it could fill the vacuum in the soil pipe without passing through the fixture and trap seal, and in some cases the device actually does protect the seal. But, as already stated, it was soon found unre-

liable on account of friction, clogging, sagging, and leaking, and because of its action in evaporating out the water seal.

In our diagram (Figure 2) you see how this evaporating action takes place. The air of a house being warmer in winter than the outer air, the ventilating current rising through the pipe in the direction shown by the arrows is conducted over or near the crown of the trap and escapes at the roof. In summer the reverse movement takes place, with a similar result. This current evaporates out the trap seal with a rapidity proportioned to its proximity to the trap, its dryness, tem-

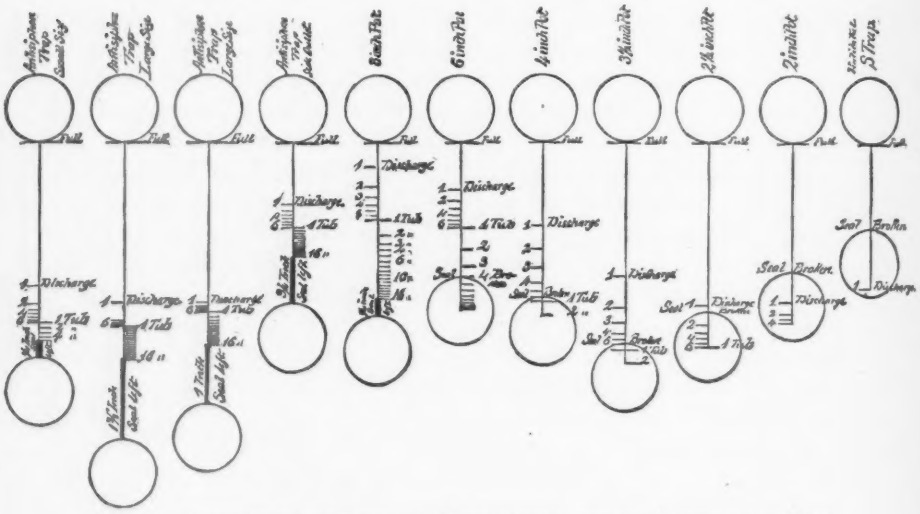

FIG. 3. — DIAGRAMS OF THE RESULTS OF EXPERIMENTS UPON THE SIPHONAGE OF TRAPS.

perature, rapidity of movement, and, in short, in proportion to its efficiency in performing its function of ventilating the branch waste pipe and guarding the seal from siphonage; and in experiments which have been published from time to time it has been found that seals have been destroyed by this cause in actual plumbing work in less than ten days. If the vent is not connected with an S-trap at or near its crown it will not protect it from self-siphonage, hence the requirement in the Boston laws, which leads to a quick destruction of the seal by evaporation.

The diagrams (Figure 3) indicate the power of resisting siphonage possessed by various kinds of traps as tested on this apparatus. The

vertical line between the two circles shows the depth of the trap seals; the short horizontal lines the amount of water removed at each discharge from the tank.

Our next slide (Figure 4) illustrates some of the many ways in which the back-vent pipe fails in practice. Clogging with grease, as shown here over the sink trap, is very common.

At every quick bend under a vertical run of iron vent-pipe rust is certain to collect. A comparatively small amount of flaking off of rust or sediment in such a place may suffice to destroy the efficiency of the pipe.

Sagging, as shown higher up, is another frequent cause of failure. Water and sediment collect in the sagged portion, and failure is again the result. Finally, hoar frost and snow often close the upper opening of the pipe above the roof, producing again failure.

Moreover, the chances of leakage by bad jointing are evidently increased in proportion to the increase of piping, and, what is more important still, no water flush passes through the vent pipes, and there is consequently nothing to announce to the eye the presence of leaks, which may therefore do mischief before the leaks are discovered.

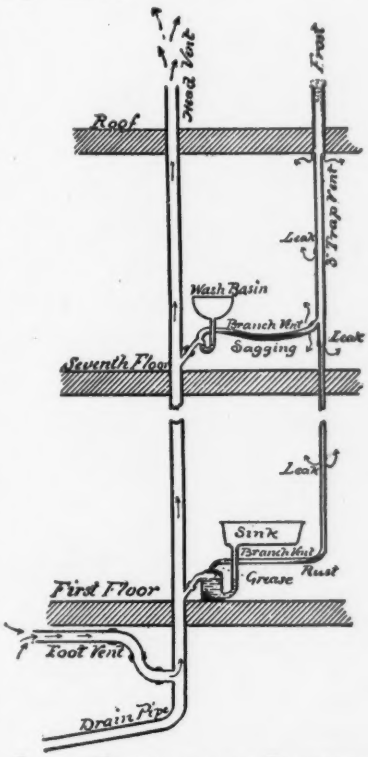

FIG. 4. — FAILURES OF THE TRAP-VENT SYSTEM IN A TALL BUILDING.

This cut, Figure 4, was used to illustrate a paper[1] on trap ventilation that I read before the Boston Society of Architects in 1891. The society then voted unanimously to make an effort to have the back-vent law repealed. A committee was appointed and counsel employed to attend to the matter. The efforts of the society, however, in this direction have not as yet met

[1] The Trap-vent Law. *Transactions Boston Society of Architects*, 1891, pp. 6–15.

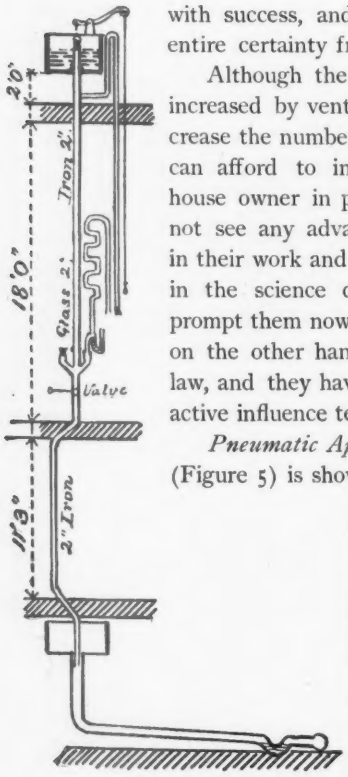

FIG. 5. — APPARATUS USED TO MAKE TESTS ON SIPHONAGE AT THE NORTH END UNION, 1902.

with success, and they have not as yet ascertained with entire certainty from what source the opposition came.

Although the amount of rough work in plumbing is increased by venting, yet the great expense tends to decrease the number and quality of fixtures which the public can afford to install, and reduces the confidence of the house owner in plumbing in general, so that plumbers do not see any advantage to themselves in the law. Pride in their work and a knowledge of the great advances made in the science of plumbing since the law was enacted prompt them now to advocate a change. The pipe dealers, on the other hand, appear to be the only gainers by the law, and they have, no doubt, constituted a powerful and active influence tending to its perpetuation.

Pneumatic Apparatus for Testing. — On the next slide (Figure 5) is shown the apparatus used to make the tests on siphonage made at the North End Union in 1902 to illustrate a series of lectures that I delivered on sanitary engineering. Slide Figure 5*a* gives the apparatus used in the Worcester tests before the Master Plumbers' Association, made soon after the Board of Health experiments were published, and in

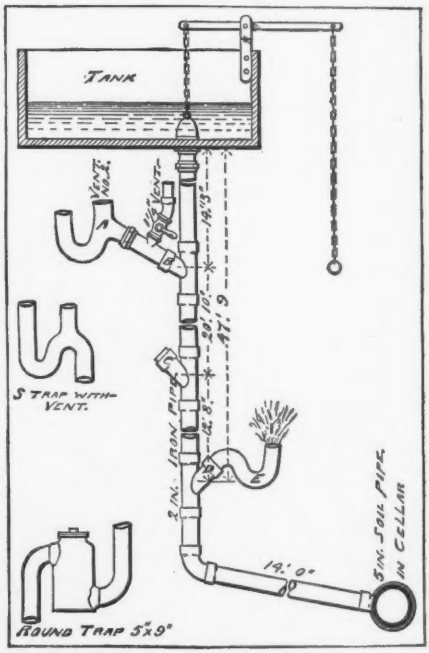

FIG. 5*a*. — APPARATUS USED IN THE WORCESTER TESTS BEFORE THE MASTER PLUMBERS' ASSOCIATION.

our next slide (Figure 6) is the apparatus that I used in a lecture at this Institute of Technology in 1885.

In these and all other demonstrations in siphonage of which I am aware, the tests have been made by hydraulic apparatus, but I have recently found that a pneumatic apparatus permits of a much greater accuracy of determination, especially in making comparative tests.

By using a suction pump we are able to reproduce at will any

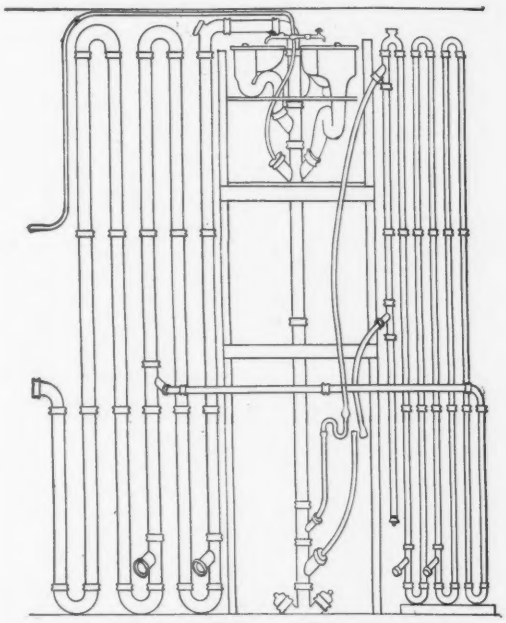

FIG. 6. — APPARATUS USED IN 1885 AT THE INSTITUTE OF TECHNOLOGY TO ILLUSTRATE SIPHONAGE.

degree of rarification desired in the soil pipe to correspond with the varying conditions encountered in plumbing practice, and a vacuum gauge enables us to apply precisely the same degree of vacuum to every trap tested, so that results of great accuracy and scientific value are obtainable. Figure 7 illustrates this apparatus.

Of course it will be objected, at first thought, that the pneumatic test does not reproduce in actual form the precise phenomena encountered in plumbing work, but a little reflection will show that the results are identical so far as they affect our inquiries. The agency which

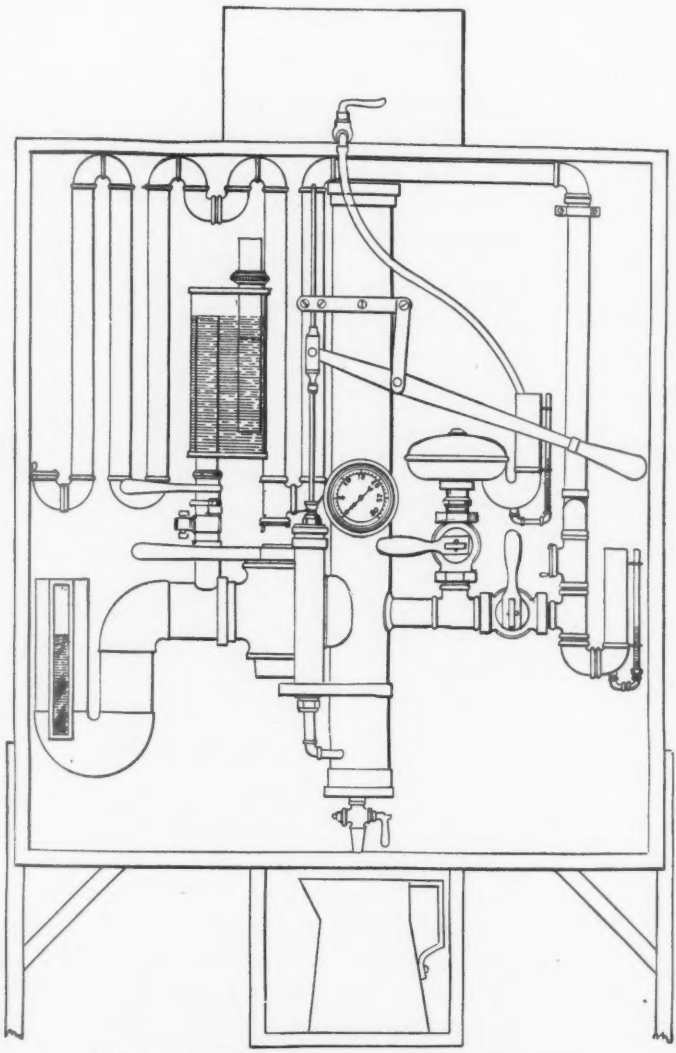

FIG. 7.—PNEUMATIC APPARATUS FOR TESTING TRAPS.
Exhibited before the Society of Arts, November 10, 1904.

produces siphonage is the partial vacuum in the soil pipe, and this rarification is effected by the rapid movement of a piston. Whether the piston be in the barrel of a pump or whether it be in the soil

pipe itself is altogether immaterial so far as concerns the effect of the partial vacuum on trap seals. The pneumatic apparatus possesses the great advantage over the hydraulic of enabling us to vary the force of the strain applied to the traps to any extent desired, while only one degree of rarification can be obtained by the falling water plug in any one plant. The siphoning action in both cases is exceedingly rapid, almost instantaneous. In the case of the falling water piston, the action takes place in the flash of time required for the piston to pass by the small mouth of the branch waste pipe serving the trap. A fraction of a second suffices for this. In the case of the air-pump apparatus the speed of the action is measured by the time it takes to move the valve lever connecting this branch waste pipe with the soil pipe. This also requires but a fraction of a second, and the speed may be regulated to correspond accurately with the hydraulic action. Moreover, a vacuum gauge may be applied to the soil pipe in both kinds of apparatus, and thus the action may be proved to be in both cases identical in speed, power, and effect.

In order, however, to satisfy the audience as to the similarity of the effect produced on the gauge and trap seals, I have had erected for this occasion both kinds of apparatus, and I shall show you that, when the vacuum gauge registers the same degree of rarification in both soil pipes, the effect on the traps in each is the same. Above the cornice I have

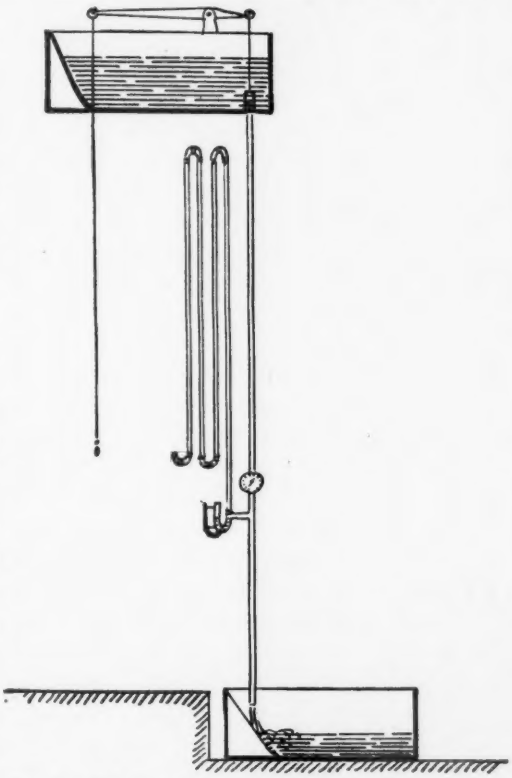

FIG. 8. — HYDRAULIC APPARATUS USED FOR EXPERIMENTS BEFORE THE SOCIETY OF ARTS, NOVEMBER 10, 1904.

had erected an ordinary bath tub (Figure 8) which now stands full of water, and at a height which nearly corresponds to two stories of an ordinary dwelling. Its overflow opening has been corked up, as is sometimes done by careful tenants, who imagine they thereby make doubly sure the exclusion of "deadly sewer gas" from the bath room. We will discharge part of the water by opening the bath plug into the waste pipe, which in this case descends in a vertical line. Having no soil-pipe connection in this hall, I have placed another bath tub below to take the place of a soil pipe in receiving the discharges.

Our branch waste here represents the waste pipe of, say, another bath tub or of a wash basin having this ordinary S-trap under it. The trap is sealed with water and is back-vented, as you see, although the vent pipe is not so long as is sometimes found in houses, varying from 30 to 300 feet in height. But to more than offset this disadvantage I have applied a larger number of bends than is usually found in practice.

Before testing the trap we will ascertain by the vacuum gauge the degree of rarification in the drain pipe obtainable by a discharge of water under these conditions from the tub.

The gauge has registered 10 inches. We cannot alter this degree of vacuum materially on this apparatus, however often we apply the test.

We will now apply this strain to the S-trap vented by 28 feet of $1\frac{1}{2}$-inch new vent pipe with four return bends. The vent pipe is new and clean, so that the conditions are in this respect favorable for it to protect the trap.

When we open the valve you see the trap has failed. The water seal in the trap has offered less resistance to the inrushing air than the friction along the walls of the vent pipe, and so the water has been driven out of the trap and the seal has been broken. The vacuum gauge registered $1\frac{1}{2}$ inches. The supply of air through the trap has lowered the vacuum from 10 to $1\frac{1}{2}$ inches.

The published records of all the tests referred to in connection with Figures 2, 5, 5*a*, and 6 have demonstrated conclusively the same thing, namely, that the S-trap vented in the manner required by the law is incapable of withstanding under all conditions the strains of siphonage which may be encountered in actual plumbing work, even when the vent pipe is new and clean and properly applied. They all corroborate the results that you have just witnessed here.

Let us now bring to bear the same amount of strain upon our trap

tested on the pneumatic apparatus (Figure 7) by rarifying the air in the soil pipe until the vacuum gauge registers the same degree of vacuum in each case as it has on our hydraulic apparatus, and we shall find the effect identical.

Before testing the traps on either plan we have ascertained the degree of vacuum which it is possible to obtain in the soil pipe by the falling plug of water or by the pump, by corking up the trap openings. In this manner we have obtained a vacuum of 10 inches on our hydraulic apparatus, and as high as 26 inches on our pneumatic, the last being a strain which is undoubtedly much severer than could ever be encountered in plumbing work. But it is very valuable in enabling us to make the most useful comparative tests, giving valuable results otherwise unattainable.

Our vent pipe is so arranged in our pneumatic apparatus (Figure 7) that we can obtain any length of vent and any number of bends we desire by simply opening or closing the little valves on the bends at different points in the length of the pipe. We have limited the length of the pipe to $10\frac{1}{2}$ feet, and the number of return bends to the equivalent of nine, because we find this will create friction enough to break the seal of a vented S-trap under a strain of less than an inch on the vacuum gauge. On the other hand, we find that we can break the seal of this S-trap with a very powerful strain of, say, 20 inches, even when the vent pipe is not over 6 inches long and has but a single return bend in it, the bore of the pipe being clean and equal in diameter to that of the trap.

We see by these tests that the severity of the strain required to break the seal of the S-trap is inversely proportional to the length of the vent pipe and to the number of bends it contains.

Closing now the vent pipe wholly or in part at the upper end, as by snow or frost, we are able to break the seal still more easily, as you see.

Closing the vent pipe at the crown of the trap, as by grease or sediment of any kind, we find the seal is instantly destroyed by the feeblest strain. A partial closure here results in a reduction of the seal proportional to the amount of the closure.

Testing Anti-siphon Traps. — Having ascertained now just what degree of siphoning strain a vented S-trap can resist, we have next to compare it with various forms of unvented anti-siphon traps. If we are to be compelled to adopt so costly a method as back-venting, with

all its faults and shortcomings, we have certainly a right to demand that it shall have at least as much power of resistance as our simpler methods when all the conditions are equal and the vent pipe is new and clean.

The tests I am going to show you now demonstrate that the back-vent system is not only not equal to the anti-siphon trap system in power of resistance, but that it is so far inferior to it as to be altogether out of competition, even with the poorer forms of anti-siphon traps.

Let us first try the ordinary "round," or "pot," trap, of which I have here samples in several sizes with glass faces so that you can see the results of the tests through these windows. The depth of seal is the same in all, namely, $4\frac{1}{2}$ inches.

We have, as you have seen, applied to these traps the severest strains that our apparatus can produce, which is a vacuum of 26 inches; and we find the large sizes capable of resisting even this strain many times repeated. Indeed it is practically impossible to siphon out our 5-inch pot trap. The first application of the strain lowers the seal considerably, but subsequent applications without refilling have little effect upon it; and when the seal has been lowered to about half an inch, practically no further reduction can be attained, however often the strain is repeated.

Our 4-inch and 3-inch pot traps have a lower resisting power, but are practically unsiphonable in plumbing work so long as they remain clean. They are thus immeasurably superior to the vented S-trap.

We find their power of resistance to be directly proportional to their diameter, and that it has nothing to do with their depth of seal.

To illustrate this law in trap construction, I have made a number of samples of bottle traps with glass bodies for experimental purposes. One of them, 5 inches in diameter, is shown in Figure 7 on the left-hand side of the soil pipe, above the pump. This trap has a seal 6 inches deep, but the depth of seal may be diminished at will by drawing up the inlet pipe through the stuffing box just above the top of the trap. By this device we can demonstrate in a very simple manner the truth of our law of trap resistance.

Nevertheless, although the ordinary unvented pot or anti-siphon trap is infinitely superior in all ways to the vented S, yet it has the one grave objection that it is not in all cases perfectly self-cleansing. Figures 9, 10, and 11 show how sediment will collect in these traps, ultimately converting them into S-traps. The mouth of the vent pipe (Figure 9)

is shown at the crown, and never having received a scour by the flushing, it is precisely the place where the floating, greasy matters and fatty vapors most quickly collect. Thus this trap loses its efficiency sooner than do the cesspool traps. The body of the S-trap is self-cleansing so long as a good flush is provided. Is it possible to obtain an anti-siphon trap which shall possess this quality of the S? If so, our trap must be

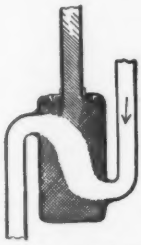

FIG. 9. — VENTED POT-TRAP BADLY CLOGGED.

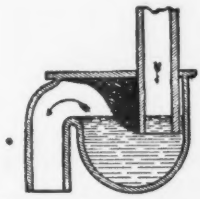

FIG. 10. — ANTI-SIPHON Ʊ-TRAP CONVERTED INTO AN S-TRAP BY DEPOSITION OF FILTH.

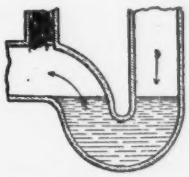

FIG. 11. — S-TRAP WITH VENT-PIPE CLOGGED, BUT BODY CLEAN.

so formed that its sectional area shall in no place exceed the area of the waste pipe from the fixture which it serves. This requirement confines us to the use of some form of plain piping, either straight or bent, in the construction of the trap. It is evident, also, that a considerable amount of this piping will be required in the formation of the trap in order to provide the necessary water capacity for resistance to back pressure and evaporation; and all the piping used must be on a horizontal plane in order to preserve the required minimum depth of water seal, as will be explained directly.

The first form of trap answering to these requirements is shown in Figure 12 — 10. It consists of a $1\frac{1}{2}$-inch S-trap seal proper and a long horizontal body made of a plain round $1\frac{1}{2}$-inch pipe. Opposite the trap proper is the sewer connection piece, also made of a bent $1\frac{1}{2}$-inch pipe. I call the long body the reservoir chamber.

The water lies along the lower half of this chamber, leaving room under siphonage for air to pass above it without disturbing the water below, provided the siphoning action is not too severe. The action is shown in Figure 12 — 7. Less and less water is driven out of the trap at each siphoning action, because the air space above the water is each time correspondingly enlarged, and the resistance to siphonage is accordingly increased until a point is reached when no further reduction of the water level by siphonage is possible. The water spray caused by the suction adheres to the long body while air escapes.

Nevertheless, this form is too long and unwieldy to be practicable. Moreover, under strong siphonage waves are formed which, when they reach the top of the pipe, act like pistons in driving out the rest of the water. The wave may be broken up and the length reduced by bending the pipe back and forth on itself, as shown in Figure 12 — 9.

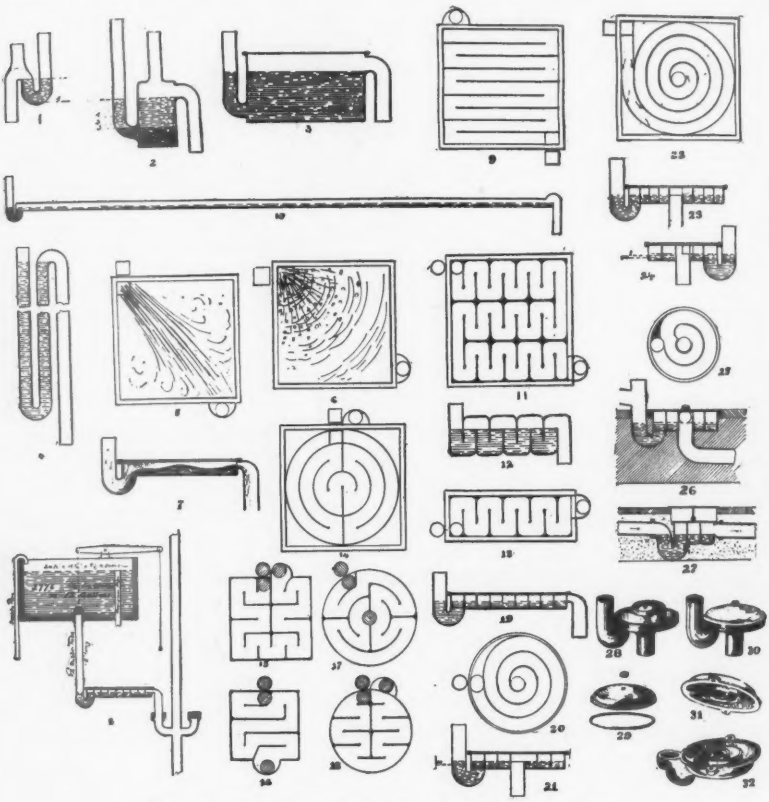

FIG. 12. — THE EVOLUTION OF AN ANTI-SIPHON TRAP.

This trap has been tested and found able to withstand indefinitely the most powerful siphonage which can be applied, a strain which in a single discharge destroyed the seal of a fully vented S-trap with a new vent pipe only 10 feet long. The same strain broke the seal of an unvented 4-inch pot trap and siphoned out an S-trap having a seal 6 feet deep (Figure 12 — 4).

Another arrangement of the pipe is shown in Figure 12 — 11, which may be reduced in size to Figure 12 — 12 and 13, when it will be seen, by comparing with Figure 12 — 1, to be nothing but a series of ordinary S-traps laid on their sides, and we have thus really succeeded in rendering an S-trap permanently anti-siphonic. The trap is, in fact, *vented through its own inlet pipe.*

This trap can, however, still be improved by giving it the form shown in Figure 12 — 22, in which friction is reduced and centrifugal force aids in the separation of the air from the water, leaving the latter in the trap while the former escapes.

The resisting power of this trap is now so great that we can materially reduce its size until we have the forms shown in Figure 12 — 20, 21, and 25 to 32.

Should this trap be used under a fixture having a small outlet, and therefore furnishing little or no scour, it will act like a straight pipe, and will, like it, in time suffer a diminution of its area by accumulation of greasy or gelatinous deposit along its walls. But, as in a straight pipe, the accumulations will be substantially uniform throughout, because the scour and form are uniform, and the resistance of the trap to siphonage will remain the same, because its principle of resistance thereto will remain unchanged, the enlargement of its lateral extension being greater than that of its sectional area. Should it ever be completely closed, its closure will announce itself by the simple cessation of the flow of waste water until the obstruction is removed through the clean-out cap.

On the table are the various forms of the experimental traps we have described and shown on the screen. It remains to subject the small, perfected form to the strains on our apparatus by which the other traps have been tested.

We see that this little trap has withstood the severest possible strains (repeated indefinitely) which our apparatus is capable of applying, and that it is therefore absolutely anti-siphonic.

Test of Shallow Seal Anti-siphon Trap in Protecting Water-closet Trap. — In virtue of the very shallow seal of this trap it is possible to use it as a vent for a deep seal water-closet trap, since being itself both a trap and a vent pipe it has the quality of protecting any deep seal trap with which it may be connected. It has in this the quality of the McLellan vent, the function of the mercury seal being here supplied by the water-seal itself.

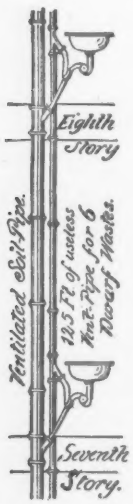

FIG. 13. — PART OF PLUMBING OF A TALL BUILDING.

You see that the deep seal trap has not been broken, even though the severest possible strain has been applied to it, for the simple reason that air to supply the vacuum in the soil pipe passes more easily through the shallow than through the deep seal, and the latter is thus protected.

This concludes our tests on the apparatus. The champions of back-venting have, as a matter of fact, abandoned today their original claim that it served to protect trap seals from siphonage. They occasionally adhere to it, however, on the argument that it is needed to purify the branch waste pipes by aëration.

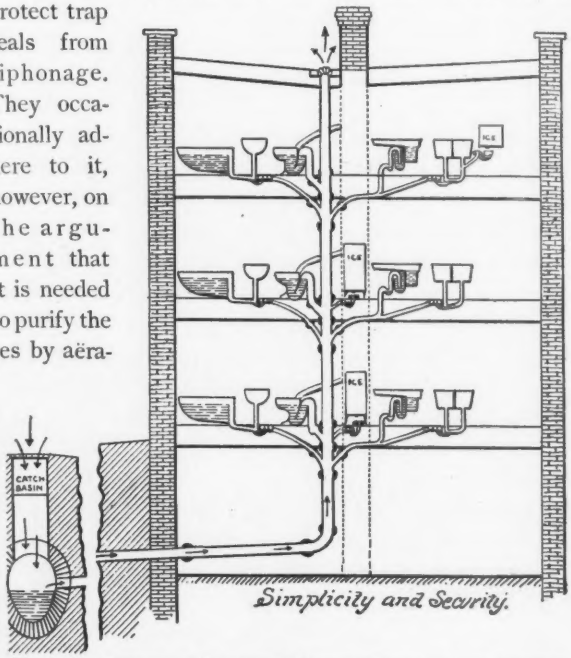

FIG. 14. — SYSTEM OF PLUMBING RECOMMENDED BY THE AUTHOR.

But it is now recognized that ample water flushing through properly constructed fixture outlets, followed by an equally thorough pure air flushing from the room through the fixture and trap, is infinitely more effective than ventilation with foul air alone from the soil pipe through the back-vent pipe, and is, indeed, altogether sufficient.

Hence the law should be that every fixture must be constructed on the principle of the "flush tank" by having outlet and outlet valves large enough to fill their waste pipes and traps "full bore" at every discharge.

Figure 13 is part of a diagram of a tall building in which, in com-

pliance with the law, I was obliged to specify trap-vent pipes 125 feet in height. As you see by the drawing, the lavatories are placed over one another in such a position that the distance from their traps to the main ventilated soil pipe is not over 18 or 20 inches. These short branch wastes were powerfully flushed at each usage of the fixtures by a stream of water filling them "full bore," and discharging at the rate of nearly half a gallon a second. Traps were specified which cannot by any possibility be siphoned out, nor have their seals seriously lowered. No better illustration of the wastefulness of this requirement could be

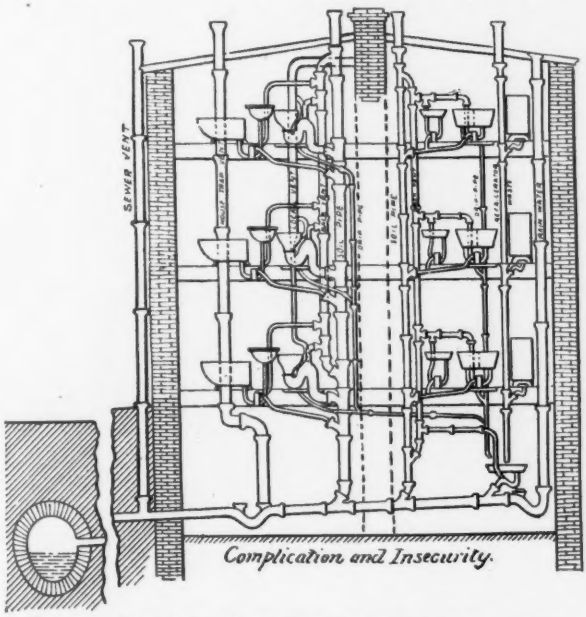

FIG. 15. — THE SAME FIXTURES WITH PLUMBING AS IN SOME FINE HOUSES. (Compare Fig. 14.)

found except in the case of alterations, where the installation of the vent pipes may destroy much valuable property and create the greatest part of the cost of the whole work.

My client in the case of this tall building lost over a thousand dollars for the privilege of seriously endangering through evaporation the seals of his traps.

In Figures 14 and 15 are shown the same fixtures in a house plumbed in two different ways, Figure 14 being in accordance with my recommendations, and Figure 15 being in accordance with the

manner now sometimes seen in the finest houses. On the extreme left of the latter is the outside sewer vent, and on the inside next to this is the house trap and circulation vent. We have also back vents, drip vents, and rain-water pipe, and all of these unnecessary stacks are very common in the modern house.

Figure 16 shows a part of this work enlarged. It is taken from a well-known house in New York. Figure 17 is taken from two other handsome New York residences, and Figure 18 from still another house in the same city.

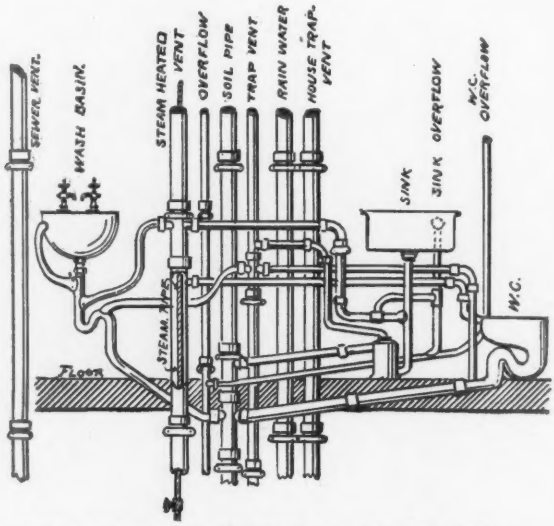

FIG. 16. — DETAILS OF PLUMBING IN A NEW YORK HOUSE.

If this absurd complication continues at the rate it has been going for the last two decades, the public will feel disposed to return to the old-fashioned method of sewage disposal shown in Viollet le Duc's picture on our next slide, where plumbing fixtures are given up altogether.

The Main House Trap. — My reasons for urging legislation prohibiting the use of the main house trap, or "intercepting" trap, are, first, because its use prevents the best and only efficient and practical method of adequately ventilating the sewers, and, second, because it adds an altogether useless expense and complication to the plumbing.

Recent investigations by eminent scientists have shown us the fallacy of the popular idea that the air of sewers abounds in disease germs, and sight-seers now visit the famous sewers of some of the great cities of the world with the same interest and safety they do the other regular "sights."

Germs are "particulate," as it was expressed by Dr. Carmichael, of Scotland, whose researches on the efficiency of a sound water seal to exclude germs are now famous among students of the subject; and they have no more power to raise themselves from the water or moist surfaces of sewers than have any other particles of vegetable matter, like leaves or small sticks. If by any chance parts of the sewage above the normal level of the flow become dried up, as in periods of drought, and are then lifted and wafted along by some unusually strong air current, it is found that they very soon fall again into the water by gravity or are carried against a wet surface in a bend or branch of the sewer by the same air current that lifted them. Furthermore, it has lately been discovered, and the discovery satisfactorily corroborated, especially by the noteworthy and most interesting researches of Laws and Andrewes, of England, that the specific germs of disease do not thrive even in the water itself of sewers. They appear to be destroyed by other species of germs, harmless to man, which do abound there.

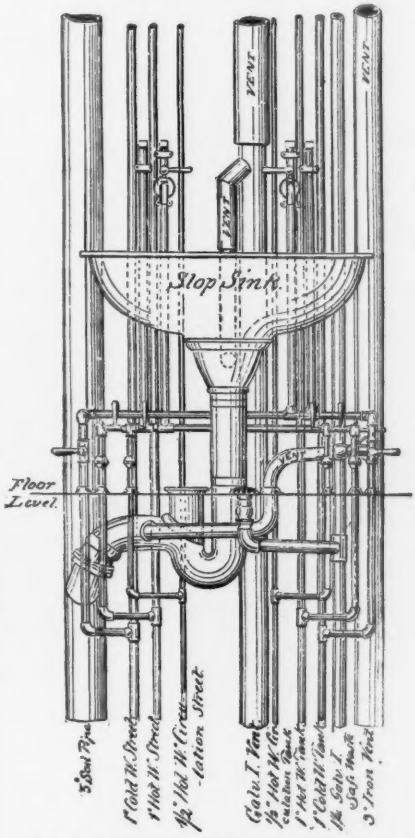

FIG. 17.—DETAILS FROM TWO HANDSOME RESIDENCES IN NEW YORK.

In short, it has been determined that the dreaded germs of diseases are, of all places, least to be sought for in the air of sewers. They may

abound in the air of the streets above the sewers, but not in that of the sewers themselves. Hence if they are borne into our dwellings by air currents at all, they must enter by way of doors and windows and not by way of the drains.

Note that we are speaking of germs and not of odors and gases. These latter do abound in the air of badly ventilated sewers and are unwholesome to breathe continuously. But they are immediately dangerous only when in an exceedingly concentrated form, and are easily excluded from houses by simple precautions and by proper plumbing.

One of the most effective and rational of these precautions is thorough ventilation of sewer and drain pipe.

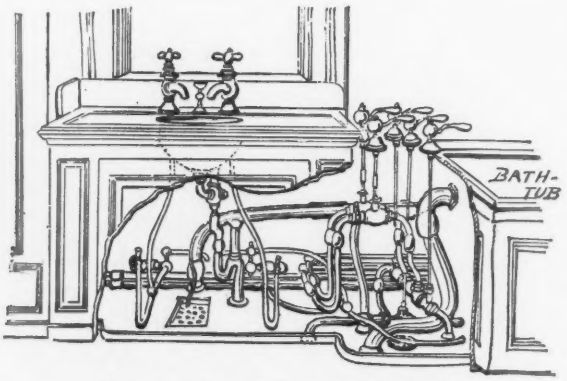

FIG. 18. — SOME BATH-ROOM PLUMBING.

In the past, sewers were sometimes ventilated by means of tall chimneys and fans and other devices built especially for the purpose at intervals in their length. But these experiments have proved failures, because they produced too powerful a suction in the immediate vicinity of the ventilators and none at all a short distance away from them, and were withal exceedingly costly.

Simple openings into the sewers at intervals along the streets are common; but they provide no motive power to effect proper ventilation. The foul sewer may thus remain foul, and an opening here and there at the street level only concentrates the nuisance in the worst manner at special places for the annoyance of the public.

It is much better to carry the foul gases to the tops of the houses than to emit them at the street level under the very noses of the

passers-by. Soil pipes can now be constructed and jointed so as to be absolutely tight, and the objection that it is dangerous to carry the sewer air through the houses is no longer tenable.

A public sewer becomes very well ventilated and practically safe when its ventilation is effected by making every house drain and soil pipe a ventilating flue. Then in cities, the sewer has special 4-inch suction tubes every 10 or 15 feet throughout its entire length, the houses averaging 20 or 25 feet in width. We know that whatever putrescible matter, excepting street washings, is to be found in the sewers comes from the house drains themselves. Assuming, then, that the houses average, say, 25 feet wide and 50 feet high, the number of running feet of soil and drain pipe in each would average at best not less than 100 feet, and the interior surface would, therefore, contain probably at least twice as much decomposing matter as the 12 feet of sewer serving each house. It would be absurd, therefore, to insert a disconnecting trap and a vast increase of extra piping for the mere purpose of excluding this small extra drain-pipe air, even if it were not demonstrated that this very complication increases, rather than diminishes, the chances of its entrance.

Even the foulest sewers and cesspools must cease to be foul the moment they are ventilated through every soil pipe. Probably the most dangerous substance in our sewers today is illuminating gas escaping from leaky mains, which modern science has, as I believe it can be maintained, at last rendered unnecessary. The house trap is responsible for the presence of this gas in cellars and subways. It is exceedingly important that when present there it should be diluted and carried up above the houses and thus rendered comparatively harmless.

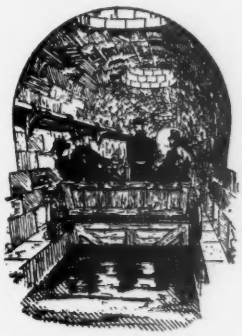

FIG. 19. — IN THE GREAT SEWER OF PARIS.

On the next lantern slide (Figure 19) is a picture of the great Paris sewer, which I inspected in 1871. I found it so clean and well ventilated that it was without any offensive odor, so much so, indeed, that hundreds of people, both ladies and gentlemen, visit it annually as one of the peculiarly interesting sights of the metropolis.

In conclusion, I will only say, in regard to calking cast-iron pipes with lead, that the law should rather prohibit this than specify it today,

in view of the very recent methods discovered of jointing cast iron scientifically and economically, permitting a certain amount of rotation and play at the joint without sacrifice to its soundness, even under pressure.

The lateness of the hour will prevent me from treating of this last matter in detail, as I had hoped to do tonight, and I know you are all eager to hear the gentlemen who have kindly consented to open the discussion and give us the benefit of their views on the subject of this legislation.

THE DECOMPOSITION AND FORMATION OF ZINC SULPHATE BY HEATING AND ROASTING.[1]

By H. O. HOFMAN.

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[1] Reprinted from the Transactions of the American Institute of Mining Engineers.

PART I. DECOMPOSITION OF ZINC SULPHATE BY HEATING IN AIR.

I. Introduction.

With the exception of lead sulphate, all common metallic sulphates are completely decomposed upon heating into metallic oxide, sulphur trioxide, sulphur dioxide, and oxygen. Some give up their trioxide readily at a low temperature, others require considerable heat and much time to be completely freed from sulphur. Kerl[1] in 1881 arranged the principal metallic sulphates as they are decomposed by a rising temperature in the following order: silver, iron, copper, zinc, nickel, cobalt, manganese, and lead; lead sulphate being decomposed only slightly at a white heat. The researches of Bradford,[2] published in 1903, show, however, that ferrous sulphate is decomposed at 590° C., cupric sulphate at 653° C., and argentic sulphate at 1,095° C. By the present investigation it will be seen that zinc sulphate is decomposed at 739° C. As far then as our present knowledge goes, the order in which the decomposition of the leading metallic sulphates takes place is the one given in Table I.

TABLE I.—Temperatures of Decomposition of Various Metallic Sulphates.

Fe	Cu	Zn	Ag_2	Ni	Co	Pb	SO_4
590	653	739	1,095	n. d.	n. d.	n. d.	°C.

Very little work has been done to determine the temperature at which zinc sulphate is decomposed, the rapidity with which the decomposition takes place, and the products that are formed. Schmieder[3] approximated the temperature of complete decomposition of zinc sulphate in a hand-reverberatory roasting-furnace treating blende by placing near the fire-bridge Seger cones and noting the one that melted when basic sulphate was converted into oxide. He estimated the temperature to be about 1,100° C.; that is, the hearth near the fire-bridge has to reach about 1,100° C., if the blende is to be satis-

[1] Grundriss der Metallhüttenkunde, Leipsic, 1881, p. 70.

[2] Transactions American Institute of Mining Engineers, XXXIII, p. 50.

[3] Oesterreichisches Jahrbuch, 1889, p. 393.

factorily dead-roasted. As to the time required for decomposing zinc sulphate, it is known in a general way that the dead-roasting of blende is a lengthy operation on account of the difficulty of decomposing the last of the sulphate. Eichhorn,[1] in connection with roasting blende in a muffle furnace, calls attention to the fact that it is not so much temperature as time that is required to obtain satisfactory results. In regard to the products formed, Vogel,[2] as early as 1814, brought normal zinc sulphate to a red heat and obtained a product insoluble in water which contained sulphur. He called it basic sulphate. Plattner[3] says that in roasting blende there is formed, beside the normal sulphate, a basic sulphate of definite chemical composition, the tetrabasic sulphate $3\,ZnO, ZnSO_4$, and that while the former is readily decomposed upon raising the temperature above the normal for roasting into ZnO, SO_3, SO_2, and O, the basic salt requires a white heat for the complete elimination of sulphur. Plattner is the only investigator who gives a basic salt formed by heating normal sulphate a definite formula. The present investigation makes it probable that, in decomposing zinc sulphate by heat, the sulphur trioxide passes off gradually and that no definite basic compound is formed.

A series of basic salts crystallizing with various amounts of water has been isolated from solutions, but they have no bearing on the work in hand.

Some of the preliminary work in this investigation was done by Messrs. W. A. Dorey and R. P. Roberts in 1900. It was carried further in 1901–02 by Mr. A. C. Dart, Jr., who tried to prove or disprove, by heating zinc sulphate in a current of air and of carbon dioxide, the correctness of the generally accepted statement that heating a metallic sulphate with limited access of air caused the SO_3 to split to a large extent into SO_2 and O, while with free access of air the volatile compound driven off was mainly SO_3. His results are given in Table II.

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[1] Berg- und Hüttenmännische Zeitung, 1889, p. 113.

[2] Journal für Chemie und Physik (edited by J. S. C. Schweigger), 1814, XI, p. 416.

[3] Die Metallurgischen Röstprocesse, Freiberg, 1856, pp. 87, 142.

TABLE II. — RESULTS OF HEATING ZINC SULPHATE WITH AND WITHOUT EXCESS OF AIR.

Heated in	Temperature.	Total sulphur eliminated.	Sulphur eliminated as SO_2.	Sulphur eliminated as SO_3.	Ratio: $\frac{S \text{ as } SO_2}{S \text{ as } SO_3}$
	Degrees Centigrade	Per cent.	Per cent.	Per cent.	
Air	578	1.63	0.14	1.49	9.06
Air	584	1.79	0.14	1.65	8.26
Carbon dioxide	599	0.50	0.18	0.32	55.25
Carbon dioxide	602	0.50	0.16	0.34	47.88

In the experiments, the results of which are given in Table II, the temperature of the furnace was brought slowly to the point at which the first acid was given off, raised about 10° C., and then maintained constant for several hours. While only a very small proportion of the total sulphur was driven off in the tests, they show that in heating zinc sulphate the tendency of the salt to split into ZnO, SO_2, and O is greater when oxygen is absent than when it has free access. Schnabel[1] quotes Schlapp as having found, while decomposing zinc sulphate on a large scale by heating, that of the total SO_3 present 30 per cent. escaped as such, while the rest passed off as SO_2 and O. Investigations along this line were not further pursued, as the researches of Knietsch[2] on the formation and decomposition of sulphur trioxide by heat in the presence and absence of catalyzing agents had about covered the ground.

The present investigation was taken up in 1903. A grant by the American Academy of Arts and Sciences from the income of the C. M. Warren fund enabled me to avail myself of the assistance of Mr. R. B. Yerxa in carrying on the work.

II. ZINC SULPHATE USED.

The zinc sulphate which formed the raw material for the experiments was the chemically pure normal salt, $ZnSO_4 + 7\ H_2O$. It was analyzed for zinc by the standard sodium carbonate method, and for sulphur by precipitating with barium chloride, the zinc having been first removed to prevent any of it from being carried down by the barium sulphate. The water was found by the difference. The results of the analysis are given in Table III.

[1] Handbuch der Metallhüttenkunde, Springer, Berlin, 1904, second edition, II, p. 46.

[2] Berichte der Deutschen Chemischen Gesellschaft, 1901, XXXIV, p. 4069. Translated by Ruhoff, Mineral Industry, 1901, X, p. 605.

TABLE III. — COMPOSITION OF ZINC SULPHATE.

	By analysis.	By calculation.
	Per cent.	Per cent.
SO_3	28.78	27.84
ZnO	29.27	28.32
	By difference	
H_2O	41.95	43.84
Ratio : SO_3 : ZnO	0.9833	0.9828

The results in Table III show that the analysis gave about 2 per cent. less water than the quantity required by the formula. This difference was accounted for by the fact that the salt had been kept in a closet the temperature of which had reached sometimes 30° C. Upon close examination the crystals appeared dull, as if they had weathered. The close agreement of the two ratios of SO_3 : ZnO proves that the sulphate was the normal salt.

III. FURNACES AND PYROMETERS.

Two electric furnaces and one gas-furnace served for the heat-work. The electric furnaces were of the resistance type first suggested and used by Prof. C. L. Norton[1] in 1894, and since then commonly employed for laboratory heating purposes with temperatures up to about 1,400° C. Figure 1 represents a sketch of the tube-furnace, *D*, with gas-train, *A*, *B*, *C*. A porcelain tube, 22 inches long and 1 inch internal diameter, glazed inside only, was wound in the centre for a distance of about 8 inches with 0.5 mm. platinum wire. The platinum coil, of thirty turns about 0.25 inch apart, was coated with a thin mortar of chemically pure magnesia; the tube then covered, excepting 5 inches at the ends, with a thick mortar of calcined magnesia, *F;* this surrounded with ordinary asbestos-magnesia covering, *G;* and the whole inclosed with fluted asbestos steam-pipe covering, *H*. The sides of the furnace were firmly held together with brass ribbons in common use for covering steam-pipes, and the ends plastered over with a mixture of magnesia and water-glass to prevent the dry part of the lining from falling out. The platinum coils were coated with chemically pure magnesia to prevent them from coming in contact with the impurities

[1] Fay and Badlam, TECHNOLOGY QUARTERLY, 1900, XIII, p. 304; Norton, Iron Age, January 3, 1901, p. 22.

contained in the ordinary magnesia, as these often form clinkers which corrode the platinum wire. By leaving the ends of the porcelain tube uncovered for 5 inches, they remained sufficiently cool, when the furnace was brought to the highest temperature, to admit the use of rubber stoppers. The wires of the thermo-couple were firmly connected with the rubber stopper, *M*, at the delivery end of the tube by cutting a longitudinal slit into opposite sides, inserting a wire, and binding the whole with adhesive tape. By thus fastening the wires to the stopper, the couple, *L*, when once adjusted to be in contact with the substance

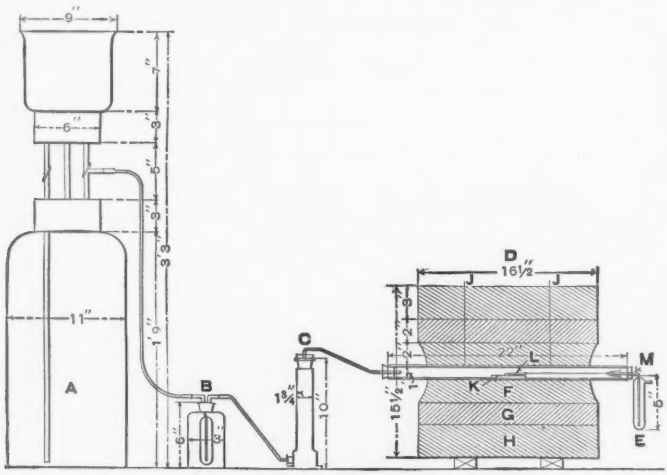

FIG. 1. — ELECTRIC TUBE-FURNACE WITH GAS-TRAIN.

in boat, *K*, to be heated, would be again in correct position when the tube was closed up after the stopper had been removed for some reason or other. The wires reaching into the tube were insulated from one another, yet, at the same time, firmly held together by winding them, over and under, with asbestos string.[1]

The gas-train consists of a gasometer, *A*, of ordinary type, used for forcing air or any other gas through the apparatus. It is followed by an Ahlin wash-bottle, *B*, filled with a strong solution of potassium permanganate, which oxidizes all traces of organic matter or sulphurous acid from the air. The drying tower, *C*, filled with pieces of calcium chloride, removes any moisture present, so that only thoroughly purified

[1] Le Chatelier and Boudouard, High Temperature Measurements. Translated by Burgess. Wiley, New York, 1901, p. 113.

and dried air can enter the porcelain tube of the furnace. At the opposite end is a railroad tube, *E*, to hold the indicator solution. It was found necessary to have two indicators. One was a very dilute solution of iodine in potassium iodide and of starch to show the presence of sulphurous acid by the fading of the blue color. As the blue color is also destroyed by organic matter, another indicator had to be provided for carbon-reduction experiments. At the suggestion of Prof. A. H. Gill, a colorless solution of potassium iodate and starch was used which was changed to blue by sulphurous acid. Carbon burned in the tube had no effect upon it.

The tube-furnace was adopted after experimenting for some time with a similar electric furnace, 16 inches long by 10 inches in diameter, the chamber of which consisted of a cylindrical clay retort, 6 inches long by 2.5 inches in diameter, the mouth being flush with the covering to admit access with tools. The furnace had to be given up for experiments requiring hermetic sealing, as it was found impossible to cement a plug into the mouth of the cylinder which would be air-tight during the experiment and permit of being easily removed at the close of a test. The retort-furnace was employed, however, in conjunction with the tube-furnace for dehydrating and for heating larger quantities of zinc sulphate than the tube could conveniently hold, under conditions not requiring the furnace to be air-tight. A gas muffle-furnace, made by the American Gas Furnace Company, New York, New York, with muffle 12 inches long by 6.75 inches wide by 3.75 inches high, was used for heating large quantities of zinc sulphate and for roasting blende.

The temperatures were measured with Le Chatelier thermoelectric couples. With the tube- and retort-furnaces a Chauvin-Arnoux galvanometer was employed, with the gas muffle-furnace the common form of Deprez-d'Arsonval. The couples were calibrated against the boiling-points of water, naphthalene, and sulphur, and the melting-points of aluminum and gold.

IV. Heating of Zinc Sulphate — Dehydration.

Manuals of chemistry teach that hydrous zinc sulphate loses six of its seven molecules of water when it is heated to 100° C.; that at a higher temperature the last molecule is driven off; and that it is difficult to remove this without at the same time starting the decomposition of the anhydrous salt. As it was important in the proposed work to

start with anhydrous salt, tests were made to find the temperature at which zinc sulphate was completely dehydrated. Weighed samples of the crystalline salt were partly dehydrated on a steam-table and then transferred to the tube-furnace. The temperature of the steam-table was about 109° C. and caused an average loss in weight of 36.29 per cent. In the tube-furnace the temperature was first brought to and maintained at 238° C. to constant weight; it was next raised to 324° C. and again held until there was no further diminution in weight. Increasing the heat did not cause any additional loss until the sulphate began to be decomposed. The temperature of approximately complete dehydration was, however, lower. Further tests at 240°, 260°, and 280° C. showed that above 280° C. there was no additional loss. Working within the limits of 260° and 280° C. it was found that 263° C. was the lowest temperature at which the last water (excepting 0.24 per cent.) was given off. With samples weighing 2 g. each it took from thirty to forty hours to finish a test. The average loss of water in the runs made at 263° C. or slightly above was 41.71 per cent., while the analysis of the salt calls for 41.95 per cent. The last 0.24 per cent. water could be set free only at a temperature at which the decomposition of the sulphate began. The losses in weight from 100° to 263° C. showed that the quantity of water driven off rose with the temperature, as did the rapidity with which it passed off.

V. Heating of Zinc Sulphate — Decomposition.

(*a*) *Beginning of Decomposition.* — Five separate experiments were carried through to determine the beginning of decomposition of anhydrous zinc sulphate. The mode of operating was as follows: A sample of the hydrous salt weighing about 3 g. was partially dehydrated on a steam-table, transferred to the tube-furnace, heated to constant weight, set aside to free the cool end of the delivery-tube completely from condensed moisture, and then replaced in the tube. In the preliminary trials it has been found that this condensed moisture absorbed the first traces of acid set free and vitiated the results. With the sample again in place and the tube closed, the air-current was started and the furnace heated, rapidly to 500° C. and then slowly. Galvanometric readings were taken as a rule every minute, often, however, at shorter intervals. When, in the slow heating, the temperature was raised 5° C. a minute, the first fading of the indicator occurred at 550° C.; when more slowly, it took place at a lower temperature. The lowest point recorded for

the beginning of decomposition on a slowly rising temperature was 532° C. Upon lowering the temperature from 532° to 525° C. and allowing it to remain constant, no fading of the indicator could be detected. When it was increased to 528° C. and held there, the indicator began to fade after about ten minutes. The decomposition of anhydrous zinc sulphate begins at 532° C. with a rising, and at 528° C. with a constant, temperature. The difference of 4° C. finds its explanation in the time required for the extremely small quantity of acid set free to travel from the boat, holding the charge, to the indicator tube. The evolution of sulphurous gas at 528° C. lasted for from one to two hours, according to the weight and the thickness of the charge. In two tests in which the salt was weighed after the sulphurous gas had ceased to be evolved, the loss in weight was only 0.04 and 0.05 per cent., based on that of the anhydrous salt, which was about 2 g. It ought to be mentioned that, after one test was finished and before another was begun, the temperature was lowered well beneath the decomposition point; also, the furnace was swept clean from any remaining free acid by a current of air.

(*b*) *Rapidity of Decomposition.* — In attempting to determine the rapidity of decomposition, it was necessary to feel one's way before any systematic work could be undertaken. A sample corresponding to 1.7535 g. of anhydrous zinc sulphate was first heated to 528° C. and kept at this temperature for 1.5 hours, when acid ceased to come off. No further decomposition took place with increase of temperature until 575° C. was reached. It took 3.5 hours of heating to separate the acid. Raising the temperature again slowly, the indicator showed the presence of acid at 610° C., and 52.5 hours passed before acid ceased to come off. As it required at the end of the 52.5 hours one whole hour's heating for the indicator to show signs of fading, the temperature was raised more quickly, 10° C. per hour, until 681° C. was reached and maintained at this stage for four hours. A further rise of 9° C. brought the charge to 690° C., at which temperature it was again held for four hours. The result of the seventy-six hours' heating was a loss of only 7.5 per cent. of SO_3 out of a possible 49 6 per cent. This decrease in weight was checked by a determination of sulphur in the residue, which was found to be 16.8 per cent. The 7.5 per cent. of SO_3 correspond to 3 per cent. of sulphur, and the anhydrous zinc sulphate contained 19.84 per cent. of sulphur. In all these tests the evolution of sulphurous acid was comparatively rapid

when a decomposition stage was reached, and then slowed down until it finally ceased altogether.

The preliminary tests having shown that with low temperatures the evolution of sulphurous acid gas was excessively slow, the subsequent tests were carried on at higher temperatures and with shorter intervals between temperature-raisings; further, the residue was weighed at the end of each heat, and thus the percentage-loss by volatilization established. Five runs were made to study the general behavior of the salt until complete decomposition, the rate of decomposition at certain temperatures, and the effect of the thickness of the charge. Table IV gives the losses in weight obtained in raising the temperatures from 528° to 836° C. in the stated time intervals. The loss in weight is very small at first; it increases, however, with the temperature. Six hours' heating at 755° C. causes a loss in weight (8.62 per cent.) far greater than seventy-two hours' heating at or slightly above 610° C. in the preceding run (7.5 per cent.). After having been kept for twenty-four hours at 755° C., the loss in weight has fallen to 1.81 per cent. (the lowest decomposition temperature is 739° C., as will be shown later on), while the total loss amounts to only 22.23 per cent. As this progress was too slow, the temperatures were raised more quickly.

TABLE IV. — Losses in Weight by Heating Zinc Sulphate.

[Charge : 1.9562 g. of zinc sulphate in a 3-inch boat.]

Time of each heat.	Temperature.	Loss of SO_3 in each heat.	Total loss of SO_3.
Hours	Degrees centigrade.	Per cent.	Per cent.
1	528	0.04	0.04
4	618	0.46	0.50
6	636	2.19	2.69
6	755	8.62	11.31
6	755	6.95	18.26
6	755	2.16	20.42
6	755	1.81	22.23
6	760	2.27	24.50
3	768	1.67	26.37
3	785	2.72	28.11
3	792	4.83	32.94
3	803	5.50	38.44
3	815	5.08	43.52
3	826	4.71	48.23
3	836	1.27	49.50

Table V gives the results of the tests made at 836° C., the highest temperature reached in Table IV, varying the thickness of the charge by spreading the same weight of ore over a 3-inch and a 6-inch boat, which gave layers 0.25 inch and $\frac{1}{16}$ inch in thickness. The 3-inch boat was heated in the tube-furnace, the 6-inch boat in the retort-furnace. The results are plotted in curves *A* and *B* of Figure 2.

TABLE V.— Losses in Weight of Zinc Sulphate Heated to 836° C.

Charge: 2.255 g. $ZnSO_4$ in a 3-inch Boat.			Charge: 2.259 g. $ZnSO_4$ in a 6-inch Boat.		
Time.	Loss SO_3.	Loss S (calculated).	Time.	Loss SO_3.	Loss S (calculated).
Hours.	Per cent.	Per cent.	Hours.	Per cent.	Per cent.
1	13.60	5.44	1	19.78	7.91
2	18.57	7.43	2	26.37	10.55
3	20.68	8.27	3	32.70	13.08
4	23.14	9.26	4	38.98	15.59
5	25.79	10.28	5	44.58	17.83
6	27.64	11.07	6	47.74	19.10
7	30.04	12.02	7	48.64	19.46
8	32.09	12.84	8	49.11	19.64
9	34.06	13.62	9	49.50	19.80
10	35.90	14.36	10	49.61	19.84
11	37.93	15.17	11	49.79	19.91
12	39.72	15.88	12	49.96	19.98
13	41.45	16.58			
14	42.83	17.13			
15	44.16	17.66			
16	45.10	18.04			
17	46.00	14.40			
18	46.59	18.64			
19	46.98	18.79			
20	47.81	19.12			
21	48.59	19.44			
22	48.86	19.54			
23	49.33	19.73			
24	49.62	19.85			
26	49.77	19.90			

Table VI gives the results of the tests made at 803° and 770° C., the salt having been spread in a 3-inch boat to a thickness of $\frac{1}{16}$ inch. The results are plotted in curves *C* and *D* of Figure 2.

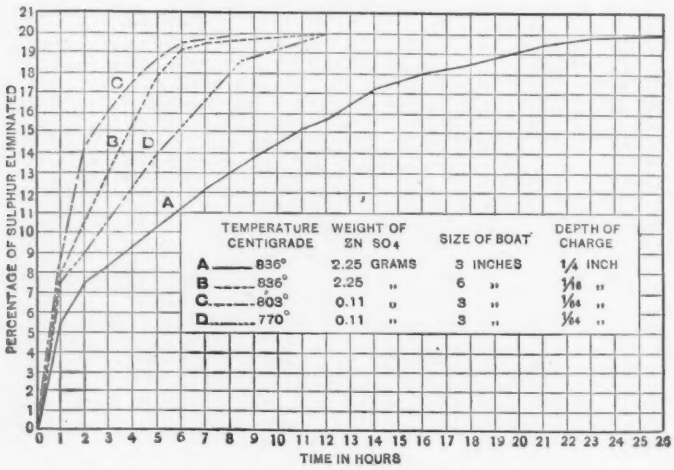
PERCENTAGE OF SULPHUR ELIMINATED
TIME IN HOURS
TEMPERATURE CENTIGRADE
WEIGHT OF ZN SO4
SIZE OF BOAT
DEPTH OF CHARGE
A ____ 836° 2.25 GRAMS 3 INCHES 1/4 INCH
B ____ 836° 2.25 " 6 " 1/16 "
C. ____ 803° 0.11 " 3 " 1/64 "
D. ____ 770° 0.11 " 3 " 1/64 "

FIG. 2. — RAPIDITY OF DECOMPOSITION OF ZINC SULPHATE.

TABLE VI. — LOSSES IN WEIGHT OF ZINC SULPHATE HEATED TO 803° C. AND 770° C.

TEMPERATURE, 803° C.			TEMPERATURE, 770° C.		
Charge: 0.109 g. of $ZnSO_4$ in a 3-inch boat.			Charge: 0.1179 g. of $ZnSO_4$ in a 3-inch boat.		
Time.	Loss SO_3.	Loss S (calculated).	Time.	Loss SO_3.	Loss S (calculated).
Hours.	Per cent.	Per cent.	Hours.	Per cent.	Per cent.
1	20.18	8.07	1.0	18.82	7.53
2	35.59	14.24	2.0	22.30	8.92
3	40.00	16.00	3.0	26.29	10.51
4	43.95	17.58	4.0	30.45	12.18
5	46.61	18.64	5.0	34.61	13.84
6	48.63	19.45	8.5	46.40	18.56
7	49.00	19.64	11.5	49.37	19.57
8	49.55	19.82	12.0	49.96	19.98

Comparing curves *A* and *B* in Figure 2, the importance of the thickness of charge upon the elimination of sulphur is brought out clearly. The charge and the temperature are the same in both cases. With a charge 0.25 inch thick (curve *A*) it takes twenty-six hours for complete desulphatization, while twelve hours (curve *B*) are sufficient to do the same work if the charge has a depth $\frac{1}{16}$ inch. The loss in

sulphur during the first hour's heating is rapid in both instances, but less so with the thicker charge (5.44 per cent.) than with the thinner one (7.91 per cent.); it then decreases gradually, again more rapidly with the thin than the thick charge. At the end of six hours the thick charge has lost 11.07 per cent. of sulphur, while with the thin charge 19.1 per cent or nearly all the sulphur has been eliminated, yet it requires six hours more to drive off the remaining traces. When, after twelve hours, the thin charge has been freed from sulphur, the thick charge has lost only 15.88 per cent., and it requires fourteen hours more heating to remove the remaining 4 per cent. of sulphur. Curves *C* and *D*, representing the heating of a small amount of salt at 803° and 770° C., are both steep; they show again the advantage of working with a thin charge, and bring out clearly the effect of difference of temperature. With 803° C. the decomposition takes eight hours; with 770° C., twelve hours. In the first hour the loss in sulphur is nearly the same, 8.07 per cent. (803° C.) and 7.53 per cent. (770° C.); the curves then diverge, the high-temperature curve rising quite rapidly as against the one of lower temperature. Comparing curve *B* (836° C., thickness of charge $\frac{1}{16}$ inch) and curve *D* (770° C., thickness of charge $\frac{1}{64}$ inch), it is seen that both charges are completely decomposed after twelve hours' heating; the elimination of sulphur at the higher temperature is more rapid in the first six hours than at the lower temperature. It requires, however, six additional hours to remove the last 0.88 per cent. of sulphur at 836° C. with a $\frac{1}{16}$-inch layer, while only two hours are necessary to do the same work at 770° C. with a $\frac{1}{64}$-inch layer.

It ought to be added that in the runs represented by curves *A*, *B*, *C*, and *D* the heating was carried on one hour longer than shown in the tables and in the figure to have proof positive that no further loss took place.

(*c*) *End of Decomposition.* — In the experiments recorded in Tables V and VI and represented graphically in Figure 2, anhydrous zinc sulphate was completely decomposed at 770°, 803°, and 836° C. It was of interest to find whether 770° C. was the lowest temperature of complete decomposition or not. For this purpose the experiments recorded in Table VII were carried out. The charge of 0.1169 g. of dehydrated zinc sulphate in a 3-inch boat was brought quickly to 763° C. and maintained for four hours at this temperature. This was done to hasten the elimination of sulphur; weighings were made hourly to note the progress. The temperature was then lowered a few degrees at a time

at half-hour intervals until no further loss in weight occurred. This took place at 730° C. The temperature was now raised to 735° C. and held there for 5.5 hours, half-hourly weights being taken.

TABLE VII.— Losses in Weight of Zinc Sulphate Heated Rapidly to 763° C.

[Charge: 0.1169 g. of zinc sulphate in a 3-inch boat.]

Time of each heating.	Temperature.	Loss in weight.	Loss of SO_3.
Hours.	Degrees centigrade.	Grams.	Per cent.
4.0	763	0.0310	26.52
0.5	752	0.0020	1.71
1.0	748	0.0032	2.74
0.5	739	0.0016	1.37
0.5	730	0.0000	0.00
5.0	735	0.0132	11.29
0.5	735	0.0000	0.00
1.0	777	0.0033	2.82
1.0	737	0.0013	1.11
0.5	737	0.0000	0.00
0.5	739	0.0014	1.20
0.5	739	0.0004	0.34
0.5	739	0.0000	0.00
0.5	749	0.0000	0.00
1.5	754	0.0000	0.00
0.5	842	0.0000	0.00

As there still remained in the residue 5.47 per cent. of sulphur trioxide, the temperature was brought to and maintained at 777° C. for one hour, to drive off the bulk of the 5.47 per cent. Table VII shows that 2.82 per cent. was thus removed. Lowering the heat to 737° C. and holding it there for one hour caused a loss of 1.11 per cent., but an additional half hour caused no further loss, although there still remained 1.54 per cent. of acid. Raising the temperature 2° to 739° C. caused in half an hour a loss of 1.2 per cent., and of 0.34 per cent. in the next half hour; a third half hour at 739° C. caused no further loss in weight, nor did heating to 749°, 754°, and 842° C. The decomposition had been completed at 739° C.; the total loss in weight was 49.1 per cent.; the time, fourteen hours. The time required for decomposing the salt completely at 739° C. was not ascertained, but, judging by the runs at 803° and 770° C., it would have been of long duration.

(*d*) *Retardation in Heating-curve.* — All the experiments so far carried out point to the conclusion that stable anhydrous basic zinc sulphates do not exist; the sulphur trioxide of the normal sulphate passes off gradually without any decided interruption, as the temperature is raised from beginning to complete decomposition. In order to verify this conclusion, the method employed by Bradford[1] in finding the temperatures of decomposition of ferrous, cupric, and argentic sulphate was applied to zinc sulphate. It consists in heating the salt slowly in contact with a thermo-couple to and above decomposition and recording the rise of temperature. Upon dissociation of the substance there will be caused a break in the heating-curve; it will be a retardation if heat is absorbed, an acceleration if set free. Zinc oxide combining with sulphur trioxide forms an exothermic reaction,

$$ZnO + SO_3 = ZnSO_4 + 52.9 \text{ kg. cal.};^2$$

hence, upon being decomposed, heat is absorbed, and the heating-curve will show a decided retardation, if all the sulphur trioxide is given off readily at a certain temperature, or if the normal anhydrous salt passes through clearly defined steps of basic salts while it is being converted into oxide.

The retort-furnace was used in the tests. It was placed on end and the retort partly filled with magnesia; a porcelain crucible charged with 5 g. of anhydrous zinc sulphate was embedded up to the rim in the magnesia. The junction of the thermo-couple was placed in the salt so as to nearly touch the bottom of the crucible. The current of 110 volts was turned on with the resistance-coils cut out. This gave at first a rise in temperature of 20° C. per minute, but it decreased, of course, as the temperature of the crucible rose. The galvanometer was read every fifteen seconds; the readings were begun at little below 528° C. and continued to above 740° C. Four separate runs were made, three with the salt in the crucible, one with the empty crucible to serve as a blank test. In the plot, shown in Figure 3, the galvanometer deflections and corresponding temperatures in degrees centigrade scale are plotted on the ordinate, and the time in minutes on the abscissa. Curve *A* represents the blank test, curves *B*, *C*, and *D* the runs made with the charged crucible. Curve *A* shows slight retardations near 747° and 790° C., which are due to irregularities of current,

[1] Transactions American Institute of Mining Engineers, XXXIII, p. 50.

[2] Berthelot, Thermo-Chimie, Paris, 1897, II, pp. 91, 305, 309.

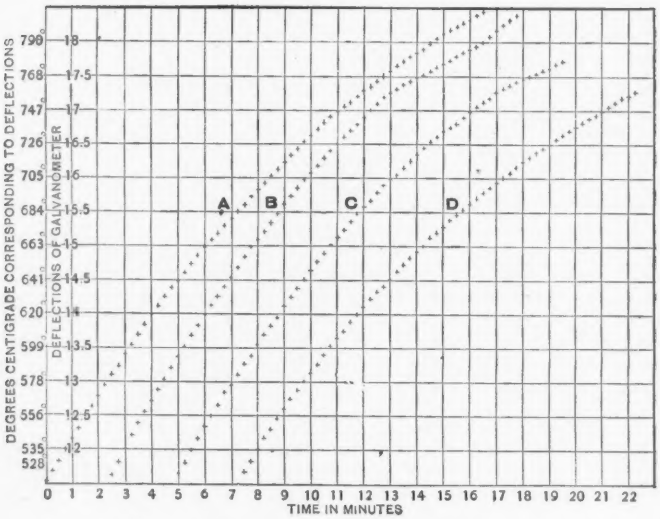

FIG. 3. — HEATING-CURVE OF ZINC SULPHATE.

caused probably by current being turned on or shut off in other parts of the Institute's laboratories. The apparent retardations in curve *B* at 760° C., and in curve *C* at 735° and 765° C., must be due to the same cause as that in curve *A*, as in curve *D* no retardation whatever is perceptible. These results, therefore, substantiate the conclusions formed from the preceding work.

(*e*) *Formation of Basic Salts.* — When anhydrous zinc sulphate, partly decomposed by heating, is treated with hot water, the undecomposed salt is quickly hydrated and dissolved, leaving behind basic salt, which dissolves with the greatest difficulty in water with continued boiling, small samples taking days of treatment. The following experiments were planned to see how much basic sulphate was formed as the decomposition of the normal sulphate and the elimination of sulphur progressed. The heating was carried on in the gas muffle-furnace. A charge of 80 g. of anhydrous normal zinc sulphate was placed in an oblong clay roasting dish, 4.25 by 10.25 inches and 0.75 inch deep, with walls 0.25 inch thick. The temperatures were taken at intervals of a few minutes by placing the thermo-couple in contact with the salt. As the top of this was found to be 10° C. lower than the bottom, the couple was pushed down toward the bottom of the tray. The charge,

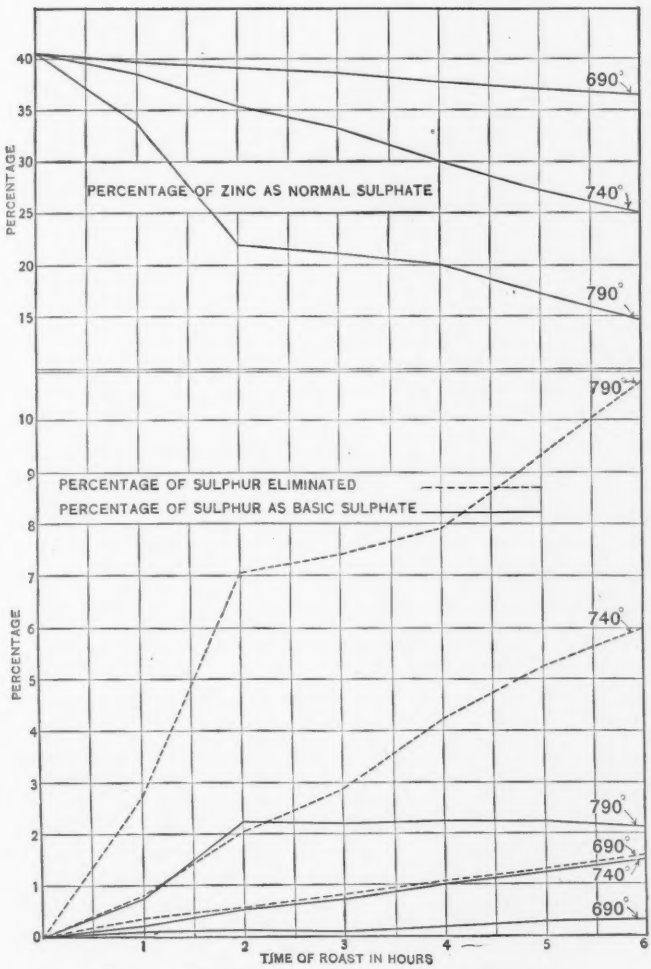

FIG. 4.—THE FORMATION OF BASIC ZINC SULPHATE.

0.5 inch in thickness, was rabbled (with a few exceptions to be noted later) at intervals of a few minutes, and samples weighing from 10 to 14 g. were taken every hour. After a sample had been obtained, the salt was pushed together so as to have the same depth as the original charge. Three heatings were made: at 790° C., or 50° C. above the lowest temperature of complete decomposition of zinc sulphate; at 740° C., the temperature of decomposition; and at 690° C., 50° C. below the final temperature. It was necessary to make on each sample three analytical determinations: the total zinc, the zinc soluble in hot water, and the sulphur insoluble in hot water.

The total sulphur eliminated was calculated by deducting from the sulphur in the charge the insoluble sulphur and the sulphur in combination with the soluble zinc sulphate. Zinc was determined by titrating with potassium ferrocyanide and the residual sulphur by dissolving the basic sulphate in the smallest possible quantity of hydrochloric acid and then precipitating with barium chloride. The total zinc-content of each sample was ascertained in order that the analytical results might be reduced to a common basis, namely, to the basis of 40.52 per cent. of zinc contained in the normal anhydrous sulphate. The results of the actual and corrected analyses, and of the calculated corrected figures for eliminations of sulphur, are given in Tables VIII (790° C.), IX (740° C.), and X (690° C.); the corrected figures are plotted in Figure 4.

TABLE VIII.—Basic Zinc Sulphate Formed by Heating Zinc Sulphate.

[Charge: 80 g. of $ZnSO_4$; temperature, 790° C.; time, six hours.]

	Actual analyses.					
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Zinc, total	43.44	48.53	48.97	49.49	52.05	54.49
Zinc as normal sulphate	36.28	26.40	25.73	24.62	22.02	19.82
Sulphur as basic sulphate	0.80	2.65	2.66	2.77	2.85	2.95
Analyses Corrected to Basis of 40.52 Per Cent. of Zinc.						
Zinc as normal sulphate	33.84	22.01	21.29	20.16	17.38	14.72
Sulphur as basic sulphate	0.747	2.21	2.20	2.27	2.25	2.14
Sulphur eliminated (calculated)	2.09	7.05	7.42	7.91	9.32	10.76

Average ratio: $\frac{\text{sulphur eliminated}}{\text{sulphur as basic sulphate}} = 3.82$

TABLE IX.—Basic Zinc Sulphate Formed by Heating Zinc Sulphate.

[Charge: 80 g. of $ZnSO_4$; temperature, 740° C.; time, six hours.]

	Actual analyses.					
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Zinc, total	40.82	42.27	43.27	44.83	45.74	46.55
Zinc as normal sulphate	38.90	36.88	35.69	33.29	31.09	29.20
Sulphur as basic sulphate	0.189	0.548	0.758	1.10	1.39	1.75
Analyses Corrected to Basis of 40.52 Per Cent. of Zinc.						
Zinc as normal sulphate	38.62	35.35	33.41	30.07	27.54	25.42
Sulphur as basic sulphate	0.188	0.525	0.709	0.997	1.23	1.53
Sulphur eliminated (calculated)	0.762	2.06	2.85	4.23	5.26	6.02

Average ratio: $\frac{\text{sulphur eliminated}}{\text{sulphur as basic sulphate}} = 4.08$

TABLE X.—Basic Zinc Sulphate Formed by Heating Zinc Sulphate.

[Charge: 80 g. of $ZnSO_4$; temperature, 690° C.; time, six hours.]

	Actual analyses.					
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Zinc, total	40.53	40.60	40.63	41.03	41.11	41.37
Zinc as normal sulphate	39.69	39.28	38.84	38.47	37.91	37.40
Sulphur as basic sulphate	0.088	0.112	0.094	0.194	0.297	0.324
Analyses Corrected to Basis of 40.52 Per Cent. of Zinc.						
Zinc as normal sulphate	39.68	39.20	38.72	37.98	37.36	36.72
Sulphur as basic sulphate	0.088	0.112	0.093	0.191	0.293	0.317
Sulphur eliminated (calculated)	0.33	0.55	0.81	1.08	1.29	1.58

Average ratio: $\frac{\text{sulphur eliminated}}{\text{sulphur as basic sulphate}} = 5.4$

The values for total zinc show readily how far the decomposition of the normal sulphate was carried. Starting with 40.52 per cent. of zinc in the original charge, the percentage has risen at the terminations of the tests with 790° C. to 54.59, with 740° C. to 46.55, and with 690° C. to only 41.37. The elimination of sulphur with 790° C. is rapid at first, slackens, and then again increases; with 740° and 690° C. it is more uniform. The total proportion driven off is, of course, greater with the higher than with the lower temperature. A

proportionality between the amount of sulphur eliminated and the degree of heat is indicated by the results at the ends of the roasts. The elimination of 10.76 per cent. at 790° C. fell to 6.02 per cent. at 740° C. and to 1.58 per cent. at 690° C.; or in a six-hour heat a difference of 50° C. in temperature made a difference of 4.5 per cent. in the sulphur elimination.

In the tube-furnace, treating small amounts at a time, it had been noticed that at any given temperature the decomposition was at first rapid and then proceeded more slowly. In the muffle-furnace this was not the case, the difference being no doubt due to the stirring of the charge.

The percentage of sulphur present as basic sulphate increases with the high temperature of 790° C. for the first three hours, remains constant up to the fifth hour, and then begins to decrease; with the lower temperatures of 740° and 690° C. it shows a steady increase. At the end of the heating the remaining percentage is higher with 790° than with 740° or 690° C. The average ratio of sulphur eliminated to sulphur as basic sulphate increases as the temperature decreases; it is 3.82 with 790°, 4.08 with 740°, and 5.40 with 640° C. The percentage of normal zinc sulphate decreases as the temperature rises. With 790° C. there is a quick fall during the first two hours, during the next two hours it is slow, and accelerates again the last two hours. With 740° and 690° it is more uniform, and, of course, greater with 740° than with 690° C.

PART II. DECOMPOSITION OF ZINC SULPHATE BY HEATING WITH CARBON (REDUCING-ROAST).

I. Introduction.

If metallic sulphates that are decomposed by heat alone are heated with a carbonaceous reducing agent, they can be partly reduced, the sulphur trioxide oxidizing the carbon. This may be expressed by the equation

$$2\ MSO_4 + C = 2\ MO + 2\ SO_2 + CO_2.$$

If the metal has more than one oxide, the higher oxide may be brought to a lower state of oxidation.

$$4\ MSO_4 + 3\ C = 2\ M_2O + 4\ SO_2 + 3\ CO_2.$$

If the metallic oxide is readily reducible, it may be partly brought to the metallic state and, combining with the sulphur, obtained by the reduction of sulphur dioxide, form a metallic sulphide.

$$2\,MSO_4 + C = 2\,MO + 2\,SO_2 + CO_2,$$
$$2\,MO + C = 2\,M + CO_2,$$
$$2\,SO_2 + 2\,C = 2\,S + 2\,CO_2,$$
$$2\,M + 2\,S = 2\,MS.$$

If the temperature is sufficiently high, the metallic sulphate is reduced to sulphide directly.

$$MSO_4 + 2\,C = MS + 2\,CO_2.$$

Reducing-roasts are not frequent now in connection with metallic sulphates; occasionally they are practiced in roasting blende carrying small amounts of galena, as the ready fusibility of galena and of some of its compounds makes it inadvisable to raise the charge to the temperature necessary for driving off all, or at least most, of the sulphur trioxide.

The only temperature measurements made in a reducing-roast are those by Scherr,[1] who found, upon addition of charcoal at 560° C. to partly roasted matte, that the 5 per cent. of soluble cupric sulphate was quickly reduced to 0.2 per cent. The first statement regarding zinc sulphate is that of Guy-Lussac,[2] who investigated the behavior of the sulphates of zinc, iron, manganese, magnesium, nickel, lead, copper, silver, and quicksilver in a reducing-roast. He found that if zinc sulphate, mixed with an excess of carbon over that required by theory, was brought in a closed vessel to a dark-red heat, there remained a residue of zinc oxide and carbon, while there passed off a gas consisting of two volumes of sulphur dioxide and one volume of carbon dioxide. If the mixture was brought quickly to a white heat, the residue was zinc sulphide and carbon, while the gas that passed off consisted of carbon monoxide, with a slight admixture of sulphur dioxide and carbon dioxide.

II: Experiments and Results.

In the experiments with anhydrous zinc sulphate there were determined the temperatures at which the reaction began and at which it became vigorous, and the residue was analyzed for sulphur. Heating

[1] School of Mines Quarterly, 1900, XXI, p. 66.

[2] Erdmann's Journal für Praktische Chemie, 1837, XI, p. 65.

was carried on in the tube-furnace. As it was necessary to carry off the volatile products of the reaction, a current of gas had to pass through the tube. Air being excluded on account of the rapid combustion of the carbon, nitrogen was used. It was prepared by Lupton's method,[1] in which ammonia gas diluted with air is conducted over a mixture of cupric oxide and metallic copper heated to redness in a small ignition-tube. The metallic copper is oxidized by the air and again reduced by the hydrogen of the ammonia. The gas mixture is obtained by forcing air through a concentrated solution of ammonia. It will be seen below, from the slow burning of the carbon in the tests, that the nitrogen thus obtained was not pure. As this did not interfere with the work, no especial pains were taken to prepare pure nitrogen. Three runs were made with six, eight, and twenty-two times as much carbon in the form of charcoal as was called for by the formula. The charge, about 0.4 g. of anhydrous zinc sulphate, was mixed and ground with the desired weight of charcoal and placed in a 3-inch porcelain boat. The mode of operating was the same as in the previous tests made in the tube-furnace.

In the first test (six times the theoretical quantity of carbon) the temperature of rapid reaction was first noted; it was 528° C. This is the temperature at which zinc sulphate begins to be decomposed when heated in air. The evolution of gas, however, was found to be much more energetic, showing that the decomposition by means of carbon at this temperature was more powerful than by means of heat alone. The temperature was then lowered; the evolution of sulphurous acid diminished correspondingly, and ceased at 475° C. The residue was white; all the carbon had been oxidized. In run Number 2 (eight times the theoretical quantity of carbon) the lowest temperature at which any sulphur dioxide could be obtained was 409° C.; it ceased after one hour's heating. Upon raising the temperature to 425° C., sulphur dioxide was again liberated, but weakly, and lasted also only for one hour. Heating at 528° C. caused the reaction to show much activity; it lasted thirteen hours; the residue was again found to be white. In order to check the results of the two preceding tests and to investigate the behavior between 425° and 528° C., a third run (twenty-two times the theoretical quantity of carbon) was made. The first sulphurous gas was again detected at 409° C.; at 463° C. carbon acted upon the sulphate, but not strongly; the effect weakened quickly and was hardly

[1] Chemical News, 1876, XXXIII, p. 90.

perceptible after 2.5 hours; at 500° C. the reaction was fairly rapid, but weakened after a few hours; at 528° C. there was the usual marked increase in the evolution of gas; the reaction continued for twenty-seven hours, weakening toward the end; all the carbon had been consumed. Upon a further addition of carbon and heating to 528° C., no further evolution of sulphur dioxide could be detected.

The weights taken in the runs were those of the anhydrous zinc sulphate, of the charcoal, and of the residue. As the percentage of ash of the charcoal had been determined, the weight of the decomposed sulphate could be easily found. The residue was analyzed for sulphide and sulphate sulphur by the method advocated by Blair.[1] The residue was dissolved in a 250-cc. decomposition-flask in a small amount of hydrochloric acid, and the hydrogen sulphide evolved conducted through an alkaline solution of lead nitrate held in a 140-cc. Erlenmeyer beaker. The hydrochloric acid solution held the sulphate sulphur, and the absorption-flask the lead sulphide precipitated by the hydrogen sulphide. The leading results of the three tests are brought together in Table XI.

TABLE XI. — Decomposition of Zinc Sulphate by Heating with Carbon.

	Test Number.		
	1.	2.	3.
Multiple of theoretical carbon	6	8	22
Time of heating — hours	7	13	27
Temperature — degrees centigrade	475	528	528
Loss in weight of $ZnSO_4$ — per cent.	6.27	30.55	42.61
Sulphide S in residue of $ZnSO_4$* — per cent.	Trace	0.61	1.41
Sulphate S in residue of $ZnSO_4$* — per cent.	17.80	6.85	2.06

* $ZnSO_4$ contains 19.86 per cent. of S.

III. Summary.

The reaction of carbon upon zinc sulphate begins at 409° C., but is weak and lasts only a short time; it grows stronger at 425°, 463°, 475°, 500° C., but weakens perceptibly after a few hours; only at 528° C. does carbon appear to become decidedly active, but even here the effect is at best very slow and imperfect, as it is opposed by the

[1] The Chemical Analysis of Iron and Steel, Philadelphia, 1901, p. 60.

direct reduction of zinc sulphate to zinc sulphide. Under the most favorable conditions the 19.86 per cent. of sulphur of zinc sulphate is diminished to 3.47 per cent.; of this total 1.41 per cent. is sulphide-sulphur and 2.06 per cent. sulphate-sulphur.

PART III. FORMATION OF ZINC SULPHATE BY ROASTING.

I. Introduction.

Blende in its deposits is usually associated with other metallic sulphides, such as galena, pyrite, marcasite, chalcopyrite, etc. If the minerals are sufficiently coarse, galena can be readily separated from blende by crushing and washing; pyrite and chalcopyrite, however, only very imperfectly. Magnetic concentration has within a few years come to the assistance of the common methods of ore-dressing and does satisfactory work. (In another paper this question is treated from a laboratory-experimental point of view.) When the metallic sulphides are very intimately mixed, ore-dressing methods fail and chemical methods come into play. The earliest of the latter class has been to give the ore a sulphatizing-roast,[1] aiming to oxidize iron and copper, and to sulphatize the lead and zinc and remove the zinc by leaching, but this has always been unsatisfactory. The only locality where it is carried on on a working-scale is at the Herzog-Julius and Frau Sophieen works in the Harz Mountains.[2] Here the leaching with water has to be supplemented by treatment with acid to dissolve basic zinc salts and zinc oxide. While no details are given as to the percentage of extraction, it may be inferred to be unsatisfactory from the fact that the slag of the blast-furnace in which the roasted and leached ore is smelted assays 19.12 per cent. of zinc. It becomes, therefore, of much value to study the conditions under which the maximum of sulphate is formed in roasting blende.

Plattner[3] is probably the earliest writer who investigated the behavior of blende when subjected to an oxidizing roast. He says that if blende,

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[1] Ingalls, Engineering and Mining Journal, May 3, 1902.

[2] Bräuning, Zeitschrift für Berg-, Hütten-, und Salinen-Wesen, in Preussen, 1877, XXV, p. 144; Kerl, Mineral Industry, 1895, IV, p. 83; Schnabel, Handbuch der Metallhüttenkunde, second edition, Berlin, 1904, p. 312; Ingalls, Metallurgy of Zinc and Cadmium, New York, 1903, p. 677.

[3] The Metallurgischen Röstprocesse, Freiberg, 1856, pp. 87, 142.

practically free from iron and in a finely divided state, is roasted with stirring at a dark-red heat, the oxidation will proceed slowly, and the sulphur dioxide evolved will be converted in part into sulphur trioxide, this process being favored by a thick bed of ore. Some of the sulphur trioxide will combine with the zinc oxide formed to yield normal sulphate and tetrabasic sulphate, and some will have an oxidizing effect upon the blende still undecomposed. If the roast is carried on at an elevated temperature and with a strong draft, causing free access of air, less sulphur trioxide will be formed and hence less zinc sulphate. If the temperature reaches the point at which the tetrabasic sulphate is decomposed, the normal sulphate cannot well form, and the result is a product containing only zinc oxide. The formation of a tetrabasic zinc sulphate has already been discussed.

The presence of iron in blende as an isomorphous sulphide is known to have a retarding influence upon the roasting of blende. Minor[1] has published interesting remarks on this point, treating four samples of blende with from 2 to 15 per cent. of Fe. His results are given in part in Table XII.

TABLE XII. — THE RETARDING INFLUENCE OF IRON UPON THE ROASTING OF BLENDE.

RAW BLENDE.		PERCENTAGE OF SULPHUR IN ROASTING BLENDE.					
No. of test.	Iron.	One hour.	Two hours.	Three hours.	Four hours.	Five hours.	Six hours.
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
1	2.33	10.32	2.86	1.80	1.71	0.95	0.08
2	13.12	24.33	21.95	20.65	17.02	2.15	0.18
3	2.06	14.69	6.27	1.23	0.22	0.16	0.06
4	15.94	27.25	24.30	18.25	11.94	4.27	0.04

The roasts are seen to have been carried very far. The behavior of the samples low in iron, Numbers 1 and 3, is normal, the percentage of sulphur falling off quickly in the first two hours, and then more slowly. With the blende high in iron, samples Numbers 2 and 4, the percentage of sulphur decreases very, very slowly, and then drops suddenly in the fifth hour; at the end of the sixth hour the blende with 15.98 per cent. (or nearly 16) of Fe contains less sulphur than any of the other three samples. An explanation for this peculiar behavior is not given.

[1] Chemiker Zeitung, 1889, p. 1602; Berg- und Hüttenmännische Zeitung, 1889, p. 446.

With regard to ferruginous blende, Jensch[1] makes the surprising statement that when roasted sweet the sulphur still present is almost wholly combined with iron as monosulphide. This is contrary to the general belief based upon practical experience and the fact that iron sulphide is more readily oxidized than zinc sulphide; contrary to the researches of Plattner,[2] who found that, under normal conditions, the iron was oxidized to ferric oxide, and that, when the temperature was very high and the access of air limited, magnetic oxide was readily formed; and contrary to the researches of Prost,[3] who finds that part of the iron oxide formed combines with zinc oxide (see Appendix, Part IV). The results of Jensch are, however, given in full in Table XIII to show that it is possible to roast dead an iron-bearing blende and leave part of the iron in the form of iron sulphide. Unfortunately, the details of operating are not given.

TABLE XIII.—JENSCH'S RESULTS OF ROASTING FERRUGINOUS BLENDE.

		Upper Silesia.			Sweden.			Erz-Gebirge.	Styria.	
		a.	b.	c.	a.	b.	c.	a.	a.	b.
		Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
I. Raw blende	Zn	32.64	22.58	32.07	31.66	35.92	32.45	44.60	44.95	42.80
	Fe	5.95	7.12	4.66	10.53	8.64	10.75	4.29	0.72	0.97
	Pb	3.12	3.20	2.88	6.88	11.10	5.38	2.50	1.12	0.85
	Mn	. .	. .	. .	. .	1.30	0.10	. .	. .	. .
II. Roasted blende	Zn	43.60	30.04	39.81	35.22	40.72	34.90	51.70	50.10	49.66
	Fe	8.11	10.00	5.73	11.78	9.17	11.62	5.12	0.84	1.16
	Pb	3.95	4.19	3.31	7.24	12.04	5.68	21.86	1.20	0.97
	Mn	. .	. .	. .	. .	1.46	. .	. .	. .	. .
III. Leached* residue from II	Zn	0.42	0.30	0.58	0.26	0.46	0.18	0.22	. .	0.18
	S	1.64	1.83	2.02	1.30	2.40	1.06	1.29	1.36	0.68
	ZnS	0.62	0.45	0.87	0.39	1.69	0.27	1.33	. .	0.27
	S available for iron	1.44	1.68	1.73	1.17	2.17	0.98	1.18	1.36	0.59
	FeS	3.96	4.62	4.74	3.22	5.97	2.69	3.24	0.99	1.62
IV. Sulphur calculated as in combination with	Zn	0.20	0.15	0.29	0.13	0.23	0.08	0.11	. .	0.09
	Fe	1.44	1.68	1.73	1.17	2.17	0.98	1.18	1.36	0.59
V. Proportion of	Zn : Fe	1 : 7	1 : 11	1 : 6	1 : 9	1 : 10	1 : 12	1 : 11	1 : ∞0	1 : 6.5

* Roasted blende (II) was leached with water and ammonium acetate to dissolve zinc and lead sulphate, and boiled with caustic soda to dissolve zinc oxide and silicate, leaving as residue zinc, iron, and sulphur.

The progressive desulphurization in large-scale work is discussed in detail by Ingalls in his "Metallurgy of Zinc and Cadmium," New York, 1903, pp. 45 *et seq.*, to which the reader may be referred.

[1] Zeitschrift für Angewandte Chemie, 1894, p. 50; Berg- und Hüttenmännische Zeitung, 1894, p. 299.

[2] *Op. cit.*, p. 143.

[3] Bulletin de l'Association Belge des Chimistes, X, p. 246; through Ingalls, Metallurgy of Zinc and Cadmium, New York, 1903, p. 32.

II. Description of Blende.

The experiments on the formation of zinc sulphate were made with blende from Joplin, Missouri, and from Warren, New Hampshire; some work was done with a sample from New Mexico. The analyses made are given in Table XIV.

TABLE XIV. — Analyses of Blende.

	Joplin, Mo.	Warren, N. H.	New Mexico.
	Per cent.	Per cent.	Per cent.
Zn	66.32	53.94	. . . .
Fe	0.45	8.80	13.40
S	32.54	31.37	. . . .
Pb	. . . .	3.82	. . . .
SiO_2	Not determined	0.82	. . . .
Cd	Not determined	Trace	. . . .

The Joplin blende was massive; it had the characteristic brown color and resinous luster. It was chosen on account of its freedom from gangue and iron. The mineral from Warren, New Hampshire, was the best representative of blende high in iron that could be obtained in considerable quantity. The sample was picked over at the mine to obtain the ore as pure as possible. When crushed through an 8-mesh sieve in the laboratory, it was again hand-sorted. Nevertheless, some lead remained behind, as shown by the analysis. The ore was made up of crystalline fragments; it had a brownish-black color and a luster more adamantine than resinous. The blende from New Mexico, used in a few cases to see how it differed in its behavior from Warren blende, was a concentrate. The mineral was black and had an adamantine luster. It was carefully picked over to exclude all foreign matter.

III. Outline of Operations.

The temperatures at which different specimens of blende decrepitate and ignite are of value in an investigation of the mineral; hence these were determined. The ore to be given a sulphatizing-roast was passed through 8- and 40-mesh sieves; a charge weighed from 200 to 350 g.; the roastings were carried on in the gas muffle-furnace; temperature and time were varied with the object of obtaining the maximum normal

sulphate; the temperatures were measured as in the experiments for formation of basic salts (p 348); and samples for analysis were taken at intervals of from 0.5 to 1.5 hours. Four determinations were made from each sample: total zinc, by titration with potassium ferrocyanide; total sulphur, by fusion with potassium nitrate and precipitation with barium chloride; normal zinc sulphate, by leaching with warm water (eight decantations of 20 cc. being sufficient) and titration of zinc, as in the determination of total zinc; and sulphur in basic zinc sulphate, the method of Steinbeck[1] being employed (covering of sample with sodium bicarbonate, adding enough water for solution, allowing to stand for twenty-four hours with occasional stirring, filtering, acidifying, and boiling filtrate, and precipitating with barium chloride). Beside the regular sulphatizing-roasts, special tests were made with Joplin blende by mixing it raw and dead-roasted with pyrite in order to increase the percentage of soluble sulphate. In this series all the samples taken were analyzed for normal zinc sulphate, and only those showing a maximum of soluble sulphate were analyzed for total zinc, total sulphur, and sulphur as basic sulphate.

Attention has been called by Prost[2] to the probable existence of a zinc ferrate, $ZnFe_2O_4$, formed in roasting ferruginous blende, which is insoluble in dilute sulphuric acid, and may be the cause of the unsatisfactory results obtained by sulphatizing-roasts. Several experiments were made to determine whether this compound existed, and, if this was found to be true, to find the conditions that favored its formation.

IV. Details of Experiments.

1. *Decrepitation.* — A small quantity of medium-size pieces was picked from each of the three lots of blende and crushed to pass an 8-mesh sieve. Each sample was then placed in a large boat and heated in the electric retort-furnace, with the junction of the thermo-couple in contact with the ore. The neck of the retort was kept open to permit watching the interior. The Warren blende did not decrepitate at all. The behavior of the blende from Joplin and from New Mexico was very similar, so they can be discussed together. Decrepitation began

[1] "Chemisch-Analytische Untersuchungen über die Veränderungen, welche der Mansfelder Kupferstein bei der Röstung erleidet." Zeitschrift für Berg-, Hütten-, und Salinen-Wesen in Preussen, 1863, XI, p. 123.

[2] *Op. cit.*

at 290° C. and lasted a few minutes. The temperature was then raised 10° at a time. With every rise decrepitation started again, and did not cease when the ignition-point had been reached. When it had stopped, about 25 per cent. of the charge was very fine and the rest medium coarse, but many pieces had retained about their original size, *i. e.*, they were caught on a 12-mesh sieve.

2. *Ignition-point.* — Three or more tests were made in the electric tube-furnace with each sample to fix the ignition-point. The sample was placed in a boat; the mode of operating was the same as with the beginning of decomposition of zinc sulphate. In the preliminary tests, in which the furnace was heated rapidly to locate approximately the point, the ignition-temperature was found to be about 40° C. too high. In the regular tests the furnace was brought slowly to near the ignition-point, and the temperature then raised at the rate of a degree to a degree and a half per minute. The tests on separate samples of decrepitated Joplin blende gave the ignition-points 480°, 479°, and 482°, or an average of 480° C. Of the Warren blende, which did not decrepitate, three tests were made on coarse (through 8- and on 12-mesh sieve) and three on fine (through 80-mesh sieve) material. The tests on the former gave 557°, 557°, and 556°, or an average of 557° C. as the ignition-point; the latter, 518°, 513°, and 515°, or 515° C. as an average. The difference of 42° C. is, of course, due to the fine material being more easily heated through than the coarse. The blende from New Mexico gave 535°, 531°, and 536°, or an average of 534° C.

TABLE XV. — IGNITION-POINT OF BLENDE.

	Source of Blende.		
	Joplin, Mo.	Warren, N. H.	New Mexico.
Size of blende	Coarse and fine	Fine	Coarse and fine
Percentage of iron	0.45	8.80	13.40
Ignition-point, degrees centigrade	480	515	534

Table XV shows that the ignition of ferruginous blende lies higher than when running low in iron, and that, as far as the three samples are concerned, the rise is nearly proportional to the iron, it being 4.19° C. for an increase of 1 per cent. of iron. If the samples are to be roasted, they have to be brought to above their ignition-temperatures, as none of them appeared to have been decomposed. The light Joplin

blende would have shown any outward change more readily than the two dark samples, but it looked just as bright and shiny as it did before it was heated. Something similar has been more recently noticed by Sharwood.[1]

3. *Sulphatizing-roast of Joplin Blende.* — With the ignition-point of Joplin blende at 480° C., it was thought that a satisfactory start in sulphatizing could be made at a temperature about 200° higher. Three roasts were carried out in the gas muffle-furnace at 690°, 740°, and 790° C., or 50° C. below, at, and 50° C. above the lowest temperature of complete decomposition of zinc sulphate. The results are given in Tables XVI (690° C.), XVII (740° C.), and XVIII (790° C.).

TABLE XVI. — RESULTS OF ROASTING JOPLIN BLENDE.

[Analysis: Zn, 66.32; S, 32.54; Fe, 0.45 per cent. Charge: 350 g.; size, 8-mesh; temperature, 690° C.; time, 12.5 hours.]

	Actual Analyses.								
Sample taken after	1 hour.	2 hours.	3 hours.	4 hours.	5 hours.	6.5 hours.	8.5 hours.	10.5 hours.	12.5 hours.
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Total zinc	66.85	67.67	68.70	69.98	70.82	71.02	71 03	71.55	72.06
Total sulphur	30.35	28.47	25.68	23.71	21.52	19.42	19.03	17.48	15.30
Zinc as normal sulphate . . .	0.155	0.199	0.206	0.290	0.335	0.409	0.463	0.672	0.638
Sulphur as basic sulphate . .	*	*	*	*	*	*	0.103†	0.121†	0.143†
Analyses Corrected to the Basis of 66.32 Per Cent. of Zinc.									
Total sulphur	30.09	27.90	24.73	22.47	20.15	18.13	17.76	16.20	14.08
Zinc as normal sulphate . . .	0.154	0.195	0.199	0.274	0.313	0.382	0.432	0.623	0.587
Sulphur‡ as normal sulphate .	0.077	0.098	0.100	0.137	0.156	0.191	0.216	0.312	0.294
Sulphur as basic sulphate . .	*	*	*	*	*	*	0.096†	0.112†	0.134†
Sulphur‡ as sulphide-sulphur	30.01	27.80	24.63	22.33	20.00	17.94	17.29	15.78	13.65

* Ore leached with sodium acetate which did not dissolve any basic sulphate; no sample left to repeat tests with sodium bicarbonate.

† Ore leached with sodium bicarbonate, which decomposed basic sulphate.

‡ Calculated.

With regard to Table XVI, the absence of data for basic salt during the first 6.5 hours is due to an error in manipulation, in that the samples were leached with sodium acetate after they had been freed from normal sulphate with warm water; from the remaining three samples the basic salt was extracted by treating with sodium

[1] Engineering and Mining Journal, June 23, 1904.

bicarbonate. As the samples of ore were used up and the data would have no practical value, the experiment was not repeated.

The elimination of sulphur at this low temperature is regular, but very slow, the amount having fallen in 12.5 hours from 32.54 to 14.08 per cent. The percentage of normal sulphate increases gradually and reaches its maximum with 0.623 per cent., while the basic sulphate is still increasing at the end of the test, after 12.5 hours.

TABLE XVII. — RESULTS OF ROASTING JOPLIN BLENDE.

(Analysis: Zn, 66.32; S, 32.54; Fe, 0.45 per cent. Charge: 350 g.; size, 8-mesh; temperature, 740° C.; time, fifteen hours.)

	ACTUAL ANALYSES.									
Sample taken after . .	1.5 hours.	3 hours.	4.5 hours.	6 hours.	7.5 hours.	9 hours.	10.5 hours.	12 hours.	13.5 hours.	15 hours.
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Total zinc	70.54	73.08	74.43	74.98	74.87	74.92	74.44	74.49	74.61	76.17
Total sulphur	24.79	17.22	12.66	7.75	6.28	6.16	5.70	4.72	3.96	3.47
Zinc as normal sulphate	0.108	0.315	0.733	1.23	1.56	1.27	2.13	2.42	2.78	2.35
Sulphur as basic sulphate	0.011	0.046	0.159	0.252	0.583	0.777	0.823	0.857	0.867	0.727
ANALYSES CORRECTED TO THE BASIS OF 66.32 PER CENT. OF ZINC.										
Total sulphur	23.30	15.63	11.42	6.85	5.50	5.45	5.08	4.20	3.53	3.02
Zinc as normal sulphate	0.101	0.285	0.662	1.09	1.38	1.10	1.89	2.16	2.48	2.04
Sulphur* as normal sulphate	0.051	0.148	0.331	0.545	0.690	0.550	0.945	1.08	1.24	1.02
Sulphur as basic sulphate	0.010	0.042	0.144	0.223	0.517	0.687	0.733	0.763	0.770	0.633
Sulphur* as sulphide-sulphur	23.24	15.44	10.94	6.08	4.29	4.21	3.40	2.36	1.52	1.37

*Calculated.

Table XVII shows that, with the higher temperature of 740° C., the decrease in total sulphur is more rapid than with 690° C., sinking to 4.2 per cent. after twelve hours, and to 3.02 per cent. after fifteen hours; the fall is quicker at the beginning than at the end; the low percentage of sulphide-sulphur at the end of the roast shows that the blende has been well decomposed. On account of the larger amount of sulphur oxidized the percentage of normal sulphate found is also greater than before; with the exception of the time interval between the seventh and tenth hour the increase is regular and reaches a maxi-

mum after 13.5 hours. The basic salt forms less rapidly than the normal salt and attains its maximum at the same time as the normal salt.

TABLE XVIII. — RESULTS OF ROASTING JOPLIN BLENDE.

[Analysis: Zn, 66.32; S, 32.54; Fe, 0.45 per cent. Charge, 350 g.; size, 8-mesh; temperature, 790° C.; time, seven hours.]

	ACTUAL ANALYSES.				
Sample taken after	1 hour.	2.5 hours.	4 hours.	5.5 hours.	7 hours.
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Total zinc	66.90	75.82	76.07	76.10	77.20
Total sulphur	27.27	10.49	3.10	2.16	1.16
Zinc as normal sulphate	0.049	0.170	. . .	1.38	0.93
Sulphur as basic sulphate	0.012	0.033	. . .	0.760	0.480
ANALYSES CORRECTED TO THE BASIS OF 66.32 PER CENT. ZINC.					
Total sulphur	25.28	9.17	2.70	1.88	0.997
Zinc as normal sulphate	0.047	0.152	. . .	1.20	0.799
Sulphur* as normal sulphate	0.024	0.076	. . .	0.60	0.40
Sulphur as basic sulphate	0.011	0.029	. . .	0.66	0.41
Sulphur* as sulphide-sulphur	25.24	9.06	. . .	0.62	0.19

*Calculated.

Table XVIII shows that, with a temperature of 790° C., the roast could be stopped after seven hours, the total sulphur having fallen to 0.997 per cent. and the sulphide-sulphur to 0.19 per cent. As the roast was carried on above the temperature at which the normal sulphate is completely decomposed, the maximum soluble sulphate is reached early and the total is smaller than in the preceding test. That the basic sulphate should follow a similar path was to be expected.

A difficulty encountered in leaching some of the samples which were afterward discarded may be mentioned. They were treated for a long time with hot water, the waters remaining in contact with the ore for several hours before they were decanted; the dissolved zinc was determined in the decantations obtained in twenty-four hours. After leaching five days in this manner without removing all the soluble zinc, the ore was boiled for thirty-six hours, with occasional decantations, and still some zinc salt went into solution. The explanation is found in the fact that basic sulphates are slightly soluble in hot and boiling water.[1]

[1] Vogel, Journal für Chemie und Physik, edited by J. S. C. Schweigger, 1814, XI, p. 416.

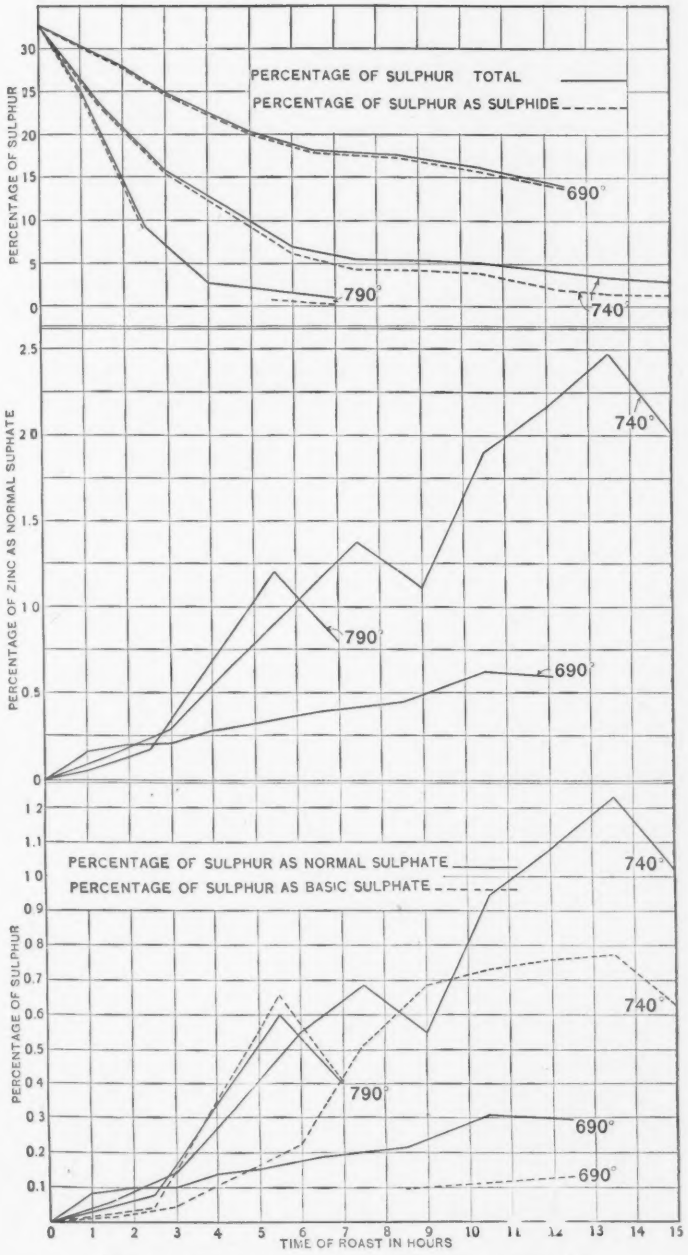

FIG. 5. — THE ROASTING OF BLENDE FROM JOPLIN, MO.

Comparing the three roasts as plotted in Figure 5, it is seen that the elimination of total sulphur increases with the temperature, while the time required decreases. The curves for sulphide-sulphur (or undecomposed blende) keep close to the curves for total sulphur, remaining, of course, below them. The narrow space between a pair of lines shows how small is the quantity of sulphate formed. The largest amount of normal zinc sulphate readily soluble in water is obtained at 740° C.; leaving out the jog in the curve at the ninth hour, the progress is quite regular until the maximum is reached, but even at best the total of normal zinc sulphate is extremely small. Basic salts, practically insoluble in water, keep an even pace with the normal salt, more so with high (790° C.) and low (690° C.) temperatures than under the favorable conditions of 740° C.

4. *Sulphatizing-roast of Warren Blende.* — The blende from Warren, New Hampshire, contains 3.82 per cent. of lead. Part of the galena is so finely disseminated through the blende that it is impossible to remove it by picking, even when using a magnifying glass. The presence of 4.41 per cent. of galena complicates matters. It is known that in roasting galena slowly at a low temperature more sulphate is formed than in roasting quickly at a high temperature;[1] hence, as far as the galena is concerned, the latter is preferable. As 690° C., with easy-roasting blende, had given a very small percentage of soluble zinc sulphate, 790° and 900° C. were chosen as roasting temperatures. The amount of lead sulphate formed is liable to be increased[2] by the sulphur trioxide set free in roasting the blende. Assuming a quick roast to take place according to the formula

$$3\ PbS + 10\ O = 2\ PbO + PbSO_4 + 2\ SO_2,$$

it is fair to suppose that the proportion of $PbO : PbSO_4$ will be as 1 : 1 at 790° C. and slightly less at 900° C. The results obtained in the two roasts are given in Tables XIX (790° C.) and XX (900° C.), and graphically represented in Figure 6.

A study of the data in Table XIX shows that the elimination of total sulphur is regular, *i. e*, quick at the beginning and slow later on, but unsatisfactory, as after fifteen hours it has been reduced to only 5.61 per cent. The percentage of normal zinc sulphate formed rises very quickly, reaches a maximum after 7.5 hours, and then falls very

[1] Hofman, Metallurgy of Lead, New York, 1899, p. 12.

[2] Plattner, Die Metallurgischen Röstprocesse, Freiberg, 1856, p. 45.

gradually. The percentages of normal and basic sulphate-sulphur apparently keep an even pace, showing that under favorable conditions for normal sulphate basic sulphate forms in considerable amounts. This explains the necessity for acid-treatment in the Harz Mountains after leaching with water.

TABLE XIX. — RESULTS OF ROASTING WARREN BLENDE.

[Analysis: Zn, 53.94; S, 31.37; Fe, 8.80; Pb, 3.82; SiO_2, 0.81 per cent.; Cd, trace. Charge: 300 g.; size, 8-mesh; temperature, 790° C.; time, fifteen hours.]

	ACTUAL ANALYSES.									
Sample taken after . .	1.5 hours.	3 hours.	4.5 hours.	6 hours.	7.5 hours.	9 hours.	10.5 hours.	12 hours.	13.5 hours.	15 hours.
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Total zinc	58.56	56.15	56.36	56.28	55.97	55.82	55.71	55.09	55.37	55.24
Total sulphur	19.56	12.58	10.79	10.07	9.75	8.66	7.93	6.65	6.42	5.96
Zinc as normal sulphate	0.597	3.76	4.41	5.06	5.08	4.74	4.68	4.37	4.21	3.95
Sulphur as basic sulphate	0.400	1.41	1.66	1.75	1.76	1.55	1.49	1.51	1.49	1.49
ANALYSES CORRECTED TO THE BASIS OF 53.94 PER CENT. ZINC.										
Total sulphur	18.02	12.09	10.31	9.65	9.40	8.37	7.68	6.51	6.25	5.61
Zinc as normal sulphate	0.550	3.61	4.22	4.85	4.89	4.58	4.53	4.27	4.10	3.72
Sulphur* as normal sulphate	0.275	1.81	2.11	2.43	2.45	2.29	2.27	2.14	2.05	1.86
Sulphur as basic sulphate	0.367	1.35	1.59	1.68	1.69	1.49	1.45	1.48	1.46	1.40
Sulphur* as sulphide-sulphur	17.34	8.93	6.61	5.54	5.26	4.59	3.96	2.89	2.74	2.35

* Calculated.

The results in Table XX show that at 900° C. the percentage of total sulphur falls in three hours from 31.37 to 1.16 per cent., and is reduced in six hours to 0.48 per cent. (= 0.16 per cent. sulphide-sulphur). The amount of normal zinc sulphate formed at this high temperature must be low; the insignificant figure of 0.228 per cent. forms the maximum, and is reached after 1.5 hours. The evil effect of a high temperature is seen by the sulphur of the basic sulphate being always higher than that of the normal sulphate, increasing up to the third hour and then diminishing.

TABLE XX.—Results of Roasting Warren Blende.

[Analysis: Zn, 53.94; S, 31.37; Fe, 8.80; Pb, 3.82; SiO_2, 0.81 per cent.; Cd, trace. Charge: 300 g.; size, 8-mesh; temperature, 900° C.; time, six hours.]

	Actual Analyses.				
Sample taken after	0.75 hour.	1.5 hours.	3 hours.	4.5 hours.	6 hours.
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Total zinc	58.06	60.43	63.66	63.96	64.48
Total sulphur	19.74	9.62	1.37	0.98	0.58
Zinc as normal sulphate	0.085	0.255	0.232	0.125	0.082
Sulphur as basic sulphate	0.266	0.433	0.527	0.450	0.340
Analyses Corrected to the Basis of 53.94 Per Cent. Zinc.					
Total sulphur	18.35	8.59	1.16	0.83	0.48
Zinc as normal sulphate	0.079	0.228	0.196	0.105	0.068
Sulphur* as normal sulphate	0.040	0.114	0.098	0.053	0.034
Sulphur as basic sulphate	0.248	0.387	0.448	0.380	0.285
Sulphur* as sulphide-sulphur	18.06	8.09	0.61	0.40	0.16

*Calculated.

A comparison of the two roasts in Figure 6 shows for 790° C. clearly the imperfect elimination of total sulphur in fifteen hours' roasting, coupled with a better formation of soluble zinc sulphate than is the case with 900° C. Lengthening the time of roasting to remove more sulphide-sulphur is, unfortunately, accompanied by a gradual but sure decomposition of the normal salt. This explains, perhaps, why it is that in the Harz Mountains it has been found necessary to roast an ore repeatedly at a low temperature to obtain any commercial extraction whatever; a single prolonged roast would give unsatisfactory results. At 790° C. the basic sulphate curve is practically always beneath that of the normal sulphate; with 900° C. just the reverse is the case.

Comparing the behavior of the Warren blende (Figure 6) with that of the Joplin blende (Figure 5), it is seen that in regard to the elimination of total sulphur, the behavior of Warren blende at 790° C. corresponds quite closely to that of Joplin blende at 740° C.; a resemblance is also to be found between Warren blende at 900° C. and Joplin blende at 790° C. In other words, the ferruginous blende gives up its sulphur less easily than the blende that runs low in iron. It may be that the geological age of the formation, as suggested by Jensch,[1] also

[1] *Loc. cit.*

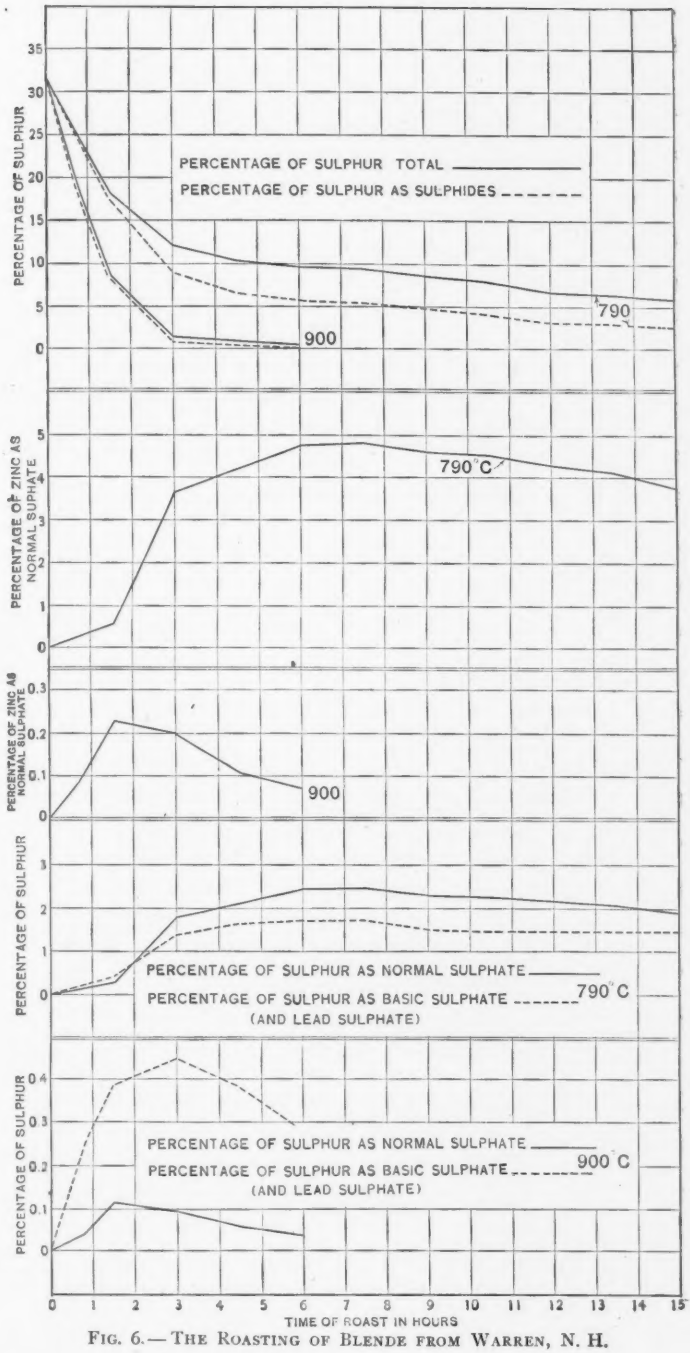

FIG. 6.— THE ROASTING OF BLENDE FROM WARREN, N. H.

has something to do with it, as Warren blende occurs in quartz-veins in Archæan gneiss, while Joplin blende is found in Carboniferous limestone. The irony blende under suitable conditions furnishes more soluble zinc sulphate than blende low in iron, and the formation extends over a longer roasting period. This is to be expected, considering that iron sulphide is converted into normal ferrous sulphate, which at 590° C. begins to be changed into ferric oxide, passing through stages of basic sulphate decomposed only at a higher temperature, all of which give off sulphur trioxide, which has an oxidizing effect upon zinc sulphide and a sulphatizing effect upon zinc oxide. The sulphatizing effect of basic iron sulphate is brought out also by the quick rate of decomposition of the soluble zinc sulphate with the Joplin blende when the maximum has been reached, in comparison with the blende from Warren. In agreement with the larger amount of normal zinc sulphate formed with blende rich in iron stands the fact that it forms more basic zinc sulphate than blende low in iron.

5. *Sulphatizing-roast with Addition of Pyrite.* — Starting with the fact proved by the preceding tests, that a ferruginous blende gave more soluble zinc sulphate than blende low in iron, it was thought that an addition of pyrite to Joplin blende might greatly improve matters, and furnish a satisfactory percentage of normal sulphate. Thus a concentrate of galena, blende, and pyrite, when subjected to a sulphatizing-roast, might furnish, after leaching with water, a desirable smelting ore of lead. Two tests were carried out, one with raw blende, the other with dead-roasted blende, to study the sulphatizing effect of pyrite under two opposite conditions. It was hoped that by furnishing to the sulphur trioxide a large quantity of zinc oxide on which it could act, a considerable quantity of soluble sulphate would be formed, as sulphur trioxide acts more strongly upon zinc oxide than upon zinc sulphide. The pyrite used came from the Davis mine in western Massachusetts. It was very pure, the analysis giving 52.95 per cent. of sulphur, or only 0.44 per cent. less than that required by the formula. In considering the quantity of pyrite to be added to the blende, the plan was to have twice the amount required by theory, *i. e.*, two parts of sulphur to one part of zinc, or 120 g. pyrite for 100 g. blende and for 83.8 g. zinc oxide. It was expected that one atom of sulphur of the pyrite starting to burn below the ignition-point of the blende would have practically no sulphatizing effect, but that the remaining monosulphide would accomplish the desired result. The temperatures chosen were 790° and 650° C., *i. e.*, above and below 740° C., the temperature at

which Joplin blende had given the maximum of soluble salt. Heating at 790° C., when zinc sulphate is rapidly decomposed, would show how much the sulphatizing effect of pyrite could counteract this tendency; while the temperature of 650° C., high enough to decompose ferrous sulphate rapidly but zinc sulphate only very slowly, would show whether with very incomplete desulphurization of blende the oxidized part would be sulphatized by the pyrite. The results are recorded in Tables XXI, XXII, and XXIII.

The data in Table XXI were obtained by roasting a mixture of blende and pyrite ground to 8-mesh size, the temperature being raised very slowly in order to avoid mechanical loss by decrepitation and to permit control of temperature when the pyrite began to burn. This occurred at about 500° C. The temperature rose in half an hour to 790° C., when the gas was shut off; it remained constant for several minutes and then began to fall, necessitating the turning on of the gas. With the ignition of the pyrite dense white fumes arose and continued for half an hour, when the pyrite ceased to glow. The first sample was taken half an hour after the ore had reached 790° C.; the others as shown in the headings. The results in Table XXI show a steady increase of soluble zinc sulphate, but after 6.5 hours the total had reached only 2.15 per cent. corrected weight; it could not have risen much higher, as the total sulphur had been reduced to 3.66 per cent.; hence the roast was not carried any farther. The total amount of sulphate, however, is twice as large as when the raw blende was roasted alone at 790° C., and that of basic sulphate very much lower; both facts show that the addition of pyrite has a beneficent effect.

TABLE XXI.—Results of Roasting Joplin Blende and Pyrite.

[Charge: 100 g. Joplin blende and 120 g. Davis pyrite; temperature, 790° C.; time, 6.5 hours. Calculated analysis: Zn, 30.14; S, 43.68; Fe, 25.43 per cent.]

SIZE OF ORE, 8-MESH.

Sample taken after	0.5 hour.	2 hours.	3.5 hours.	5 hours.	6.5 hours.
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Zinc as normal sulphate	0.42	1.00	2.19	2.33	2.70

Analysis of Ore at Maximum Normal Sulphate.

	Zinc.	Sulphur.	Zinc as normal sulphate.	Sulphur as normal sulphate.	Sulphur as basic sulphate.	Sulphur as sulphide-sulphur.
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Actual	37.83	4.59	2.70	1.35	0.831	2.41
Corrected to 30.14 per cent. of zinc	30.14	3.66	2.15	1.08	0.663	1.92

SIZE OF ORE, 40-MESH.

Sample taken after	0.5 hour.	2 hours.	3.5 hours.	5 hours.	6.5 hours.
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Zinc as normal sulphate	1.32	3.27	3.18	2.75	1.79

ANALYSIS OF ORE AT MAXIMUM NORMAL SULPHATE.

	Zinc.	Sulphur.	Zinc as normal sulphate.	Sulphur as normal sulphate.	Sulphur as basic sulphate.	Sulphur as sulphate-sulphur.
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Actual	39.92	2.85	3.27	1.64	0.868	0.34
Corrected to 30.14 per cent. of zinc	30.14	2.15	2.47	1.24	0.657	0.25

The second set of results in Table XXI was obtained by roasting a mixture of blende and pyrite ground to pass a 40-mesh screen, the other conditions being exactly the same as in the first set of experiments. This fine grinding was made in order to have a finer material and a more intimate contact between particles than was possible with the previous charge of 8-mesh grains. The effect is striking in that the maximum normal sulphate, only slightly higher than with the coarser material (2.47 per cent. *versus* 2.15 per cent.), is reached after two hours, and that the total sulphur at the same time reduced to a lower figure (3.66 per cent. *versus* 2.15 per cent.). The ratios of sulphur as basic sulphate to sulphur as normal sulphate of the 8-mesh and 40-mesh samples at maximum normal sulphate do not differ much, viz., 0.663 : 1.08 = 0.61 for the coarse, and 0.657 : 1.24 = 0.53 for the fine; they are, however, about one-half of that obtained when the 8-mesh blende is roasted by itself, and show that in the latter case much more basic sulphate is formed than in the former.

The data in Table XXII were obtained from a charge of 100 g. Joplin blende roasted dead in two hours at 950° C., the sulphur being reduced to 0.085 per cent. The roasted ore was cooled, the theoretical quantity (83.8 g.) weighed out and mixed with pyrite of 8-mesh size. The percentage of normal sulphate increased with the time of roasting. It reached, however, only 2.50 per cent. after three hours, when further heating was stopped. It could not have gone much higher by prolonging the heating, as the total sulphur had already been reduced to 2.13 per cent.

TABLE XXII. — RESULTS OF ROASTING DEAD-ROASTED BLENDE AND PYRITE.

[Charge: 83.8 g. dead-roasted Joplin blende and 120 g. Davis pyrite; temperature, 650° C.; time, three hours. Calculated analysis: Zn, 32.54; S, 31.18; Fe, 27.43 per cent.]

SIZE OF ORE, 8-MESH.

Sample taken after	1 hour.	2 hours.	3 hours.
	Per cent.	Per cent.	Per cent.
Zinc as normal sulphate	1.50	2.48	3.12

ANALYSIS OF ORE AT MAXIMUM NORMAL SULPHATE.

	Zinc.	Sulphur.	Zinc as normal sulphate.	Sulphur as normal sulphate.	Sulphur as basic sulphate.	Sulphur as sulphide-sulphur.
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Actual	40.70	2.67	3.12	1.56	0.387	0.72
Corrected to 32.54 per cent. of zinc	32.54	2.13	2.50	1.25	0.308	0.57

SIZE OF ORE, 40-MESH.

Sample taken after	1 hour.	2 hours.	3 hours.
	Per cent.	Per cent.	Per cent.
Zinc as normal sulphate	5.82	6.04	5.50

ANALYSIS OF ORE AT MAXIMUM NORMAL SULPHATE.

	Zinc.	Sulphur.	Zinc as normal sulphate.	Sulphur as normal sulphate.	Sulphur as basic sulphate.	Sulphur as sulphide-sulphur.
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Actual	37.97	4.16	6.04	3.02	1.06	0.08
Corrected to 32.54 per cent. of zinc	32.54	3.57	5.18	2.59	0.906	0.07

The conditions in this roast, given in the lower part of Table XXII, were the same as those in the upper part, excepting that the dead-roasted blende and pyrite had been crushed together to pass a 40-mesh sieve. The effect of fineness of ore and consequent intimate contact of particles is as apparent here as it was with raw blende and pyrite in Table XXI. The maximum of soluble zinc sulphate, 5.18 per cent., is reached after two hours with the total sulphur reduced to 3.57 per cent. and the sulphide-sulphur to 0.07 per cent. It is a great deal higher than with the 8-mesh mixture of Table XXII; with that some iron sulphide must have remained undecomposed, as the corrected analysis shows 0.57 per cent. of sulphur. The ratios of sulphur as basic sulphate to sulphur as normal sulphate (0.25 for 8-mesh, and 0.35 for 40-mesh mixture) are lower than those of 790° C., or a smaller amount of basic sulphate is formed at a lower temperature. The normal as

well as the basic zinc sulphate found in these tests contains a trace of iron sulphate.

In order to obtain another means of comparison for raw blende and roasted blende mixed with pyrite, a test was made with a 40-mesh mixture of raw blende and pyrite at 650° C. The total sulphur would not, of course, be reduced to a low figure; that which was set free might, nevertheless, have a strongly sulphatizing effect. The maximum soluble sulphate was obtained after 8.25 hours, 4.13 per cent. by actual, and 3.49 per cent. by corrected, analysis. The results of this experiment are given in Table XXIII. This is the second highest figure obtained in the sulphatizing tests with blende- and pyrite-mixtures, although the total sulphur has been reduced only to 13.8 per cent., and the sulphide-sulphur to 12 per cent. The sulphide-sulphur will have been, in all probability, in combination with zinc.

TABLE XXIII. — RESULTS OF ROASTING BLENDE AND PYRITE.

[Charge: 100 g. Joplin blende and 120 g. Davis pyrite; temperature, 650° C.; time, 12.75 hours. Calculated analysis: Zn, 30.14; S, 43.63; Fe, 25.43 per cent.]

SIZE OF ORE, 40-MESH.

Sample taken after	0.75 hour.	2.25 hours.	3.75 hours.	5.25 hours.	6.75 hours.	8.25 hours.	9.75 hours.	11.25 hours.	12.75 hours.
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Zinc as normal sulphate . . .	0.68	1.93	3.04	3.30	3.65	4.13	4.11	4.10	4.06

ANALYSIS OF ORE AT MAXIMUM NORMAL SULPHATE.

	Zinc.	Sulphur.	Zinc as normal sulphate.	Sulphur as normal sulphate.	Sulphur as basic sulphate.	Sulphur as sulphide-sulphur.
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Actual	35.68	16.34	4.13	2.07	0.05	14.82
Corrected to 30.14 per cent. Zn	30.14	13.80	3.49	1.75	0.04	12.00

The ratio of sulphur as basic sulphate to sulphur as normal sulphate is 0.026; that of the two preceding tests, 0.25 and 0.35. The enormous decrease is probably due to the complete decomposition of basic iron sulphates in the 8.25 hours, while the three hours of the other two roasts were not sufficient for this purpose; in none of the samples taken after 3.75 hours' roasting could any dissolved iron be detected. Between 8.25 and 12.75 hours' roasting very little soluble zinc sulphate is decomposed, the difference, 4.13 — 4.06, being only 0.07 per cent.

It ought to be stated that in all the roasts carried out at 650° C. the charge showed a tendency to rise above the given temperature as

long as pyrite was burning freely. Whenever the pyrometer indicated a rise to the danger point, the tray was removed from the muffle and allowed to cool to the desired degree of heat. After pyrite had ceased to burn, the temperature showed no tendency to rise above 650° C.

6. *Summary of Sulphatizing-roasts.* — In order to bring together the leading features of the results obtained in the sulphatizing-roasts, the main points have been assembled in Table XXIV. The conclusions arrived at are: —

TABLE XXIV. — Summary of Sulphatizing-roasts of Blende with and without the Addition of Pyrite.

	Kind of Ore.									
	Joplin blende.			Warren blende.		Raw Joplin blende and Davis pyrite.*		Roasted Joplin blende and Davis pyrite.†		Raw Joplin blende and Davis pyrite.*
Analysis of ore	Zn, 66.32% S, 32.54% Fe, 0.45%			Zn, 53.94% S, 31.37% Fe, 8.80% Pb, 3.82%		Zn, 30.14% S, 43.68% Fe, 25.43%		Zn, 32.54% S, 31.18% Fe, 27.43%		Zn, 30.14% S, 43.68% Fe, 25.43%
Weight of roasting charge, grams	350	350	350	300	300	220	220	203	203	220
Size of ore, mesh to linear inch	8	8	8	8	8	8	40	8	40	40
Temperature of roast, °C.	690	740	790	790	900	790	790	650	650	650
Time of roast, hours	12.5	15	7	15	6	6.75‡	6.75	3	3	12.75
Maximum normal zinc sulphate, after hours	10.5	13.5	5.5	7.5	2.25	6.75	2.25	3	2	7.25
Weight of leaching sample, grams	10 and 3	10	10	10	10	3	3	3	3	3
Maximum normal zinc sulphate, per cent.	0.623	2.48	1.20	4.89	0.228	2.47	2.47	2.50	5.18	3.49
Maximum basic zinc sulphate, after hours	§	13.5	5.5	7.5	3.75	§	§	§	§	§
At maximum normal sulphate. Sulphur as normal sulphate, per cent.	0.312	1.24	0.60	2.45	0.114	1.08	1.24	1.25	2.59	1.75
At maximum normal sulphate. Sulphur as sulphide-sulphur, per cent.	15.74	1.52	0.62	5.26	8.09	1.92	0.25	0.57	0.07	12.00
At maximum basic sulphate. Sulphur as basic sulphate, per cent.	§	0.77	0.66	1.69§	0.45§	§	§	§	§	§
At maximum basic sulphate. Sulphur as sulphide-sulphur, per cent.	§	1.52	0.62	5.26	0.61	§	§	§	§	§
At end of roast. Sulphur as normal sulphate, per cent.	2.94	1.02	0.40	1.86	0.034	Not determined				. . .
At end of roast. Sulphur as basic sulphate, per cent.	0.134	0.633	0.41	1.40	2.85					. . .
At end of roast. Sulphur as sulphide-sulphur, per cent.	13.65	1.37	0.19	2.35	0.16					. . .
At end of roast. Sulphur, total, per cent.	14.08	3.02	0.997	5.61	0.48					. . .
Zinc extracted, at maximum normal sulphate, per cent. on zinc in ore	0.94	3.74	1.81	9.07	4.23	7.99	8.19	7.68	15.92	11.58

* Raw Joplin blende, 100 g.; Davis pyrite, 120 g.

† Roasted Joplin blende, 83.8 g.; Davis pyrite, 120 g.

‡ Roast not carried to maximum soluble sulphate.

§ Maximum not reached.

1. The amount of normal zinc sulphate soluble in hot water obtained in the tests is very small. Based upon 100 parts of zinc in the charge, it reaches 9.07 per cent. with raw blende and 15.92 per cent. with dead-roasted mixed with a large excess of pure pyrite. Both extractions are too small to be of much practical value.

The fundamental difficulty in obtaining a satisfactory percentage of extraction lies in two facts: normal zinc sulphate is rapidly decomposed at the temperature for roasting blende; at the beginning of a roast sulphur dioxide strongly predominates over sulphur trioxide. In the process carried out in the Harz Mountains, the ore is roasted very slowly in heaps which have to be turned three times; the first heap of 500 tons of ore burns from six to seven months, the second fire lasts from six to eight weeks, and the third from four to six weeks. Normal and basic sulphates are formed mainly in the fines, *i. e.*, in the relatively cool cover, and these alone are leached with water and sulphuric acid. The probable explanation for the formation of these sulphates is that zinc sulphate formed toward the hotter centre of a heap is decomposed, and the sulphur trioxide, dioxide, and oxygen rising attack the fines in the cool cover and form normal and basic salts, or normal salts alone which are decomposed in part when the heat creeps up toward the end of the roast.

2. The ratio of sulphur as basic sulphate to sulphur as normal sulphate increases with the temperature.

3. Ferruginous (Warren) blende is more difficult to roast than blende running low in iron (Joplin), but the former gives, under similar conditions of treatment, a higher yield in normal sulphate, owing to the presence of isomorphous sulphide, the basic salts of which have a strongly sulphatizing effect when they are decomposed by heat.

Part IV. Appendix: Formation of Zinc Ferrate.

It has been proved that, in dead-roasting ferruginous blende under normal conditions, both the iron and zinc sulphides are converted into oxides. If these oxides were merely a mechanical mixture, it ought to be easy to remove all the zinc oxide by a solvent which would not attack the iron oxide; but in treating such ores, it has been found that a considerable proportion of the zinc remained in the residue. Prost[1] thinks that zinc oxide and ferric oxide form zinc ferrate,

[1] Bulletin de l'Association Belge des Chimistes, X, pp. 246–263, through Ingalls, Metallurgy of Zinc and Cadmium, New York, 1903, p. 32.

$ZnFe_2O_4$, which is not readily soluble, and Ingalls also inclines to this belief.

While this question is not directly connected with the subject in hand, it seemed of interest to make a few synthetical tests in order to find out whether such a compound was formed or not. These tests consisted in heating weighed quantities of zinc oxide and ferrous sulphate, and of zinc oxide and ferric oxide, in a porcelain crucible over a Bunsen burner, and leaching the heated mixture with ammonium sesquicarbonate. A solution of this salt was chosen instead of the pure ammonia liquor, for the reason that tests made by me years ago[1] had shown that the sesquicarbonate was an excellent solvent for ignited zinc oxide, while pure ammonia was not.

The chemically pure zinc oxide used for the tests was found to have taken up carbonic acid by long standing; an analysis gave 68.48 per cent. of zinc instead of the theoretical 80.26 per cent. Crystals of green vitriol furnished the ferrous sulphate; the ferric oxide was prepared by roasting ferrous sulphate. In order to form $ZnFe_2O_4$, the proportions of Zn : Fe required are 54 : 93. The results of the series of tests made are given in Table XXV.

TABLE XXV. — Results of Heating Zinc Oxide with Ferrous Sulphate and with Ferric Oxide.

	Experiment, Number					
	1.	2.	3.	4.	5.	6.
Proportion by weight, zinc : iron	54 : 3	54 : 9	54 : 27	54 : 93	54 : 93	54 : 9
Time of heating, hours	1	1	2	1	2	1
Time of leaching, hours	2	2	2	2	2	2
Total zinc, leached, per cent.	98.19	92.96	77.85	39.42	39.65	99.91
(*a*) Total zinc in residue, per cent.	1.81	7.04	22.15	60.58	60.35	0.09
(*b*) Total zinc, per cent. of, required to form $ZnFe_2O_4$	3.22	9.67	29.00	100.00	100.00	9.67
Ratio, $a : b$	0.56	0.73	0.76	0.60	0.60	. .

In making up the mixtures, the quantity of zinc was kept constant and that of the iron varied. The time of heating ranged from one to two hours; one hour, however, was sufficient to produce the desired result, as is seen from tests Numbers 4 and 5. Experiments in leach-

[1] Zeitschrift für Berg-, Hütten-, und Salinen-Wesen in Preussen, 1880, XXVIII, pp. 279 and 280.

ing proved that a time of longer duration than two hours gave no additional extraction, hence two hours was chosen as standard.

In experiment Number 1 the proportion by weight of zinc and iron is 54 to 3. Of the total zinc present, 98.19 per cent. was dissolved out, leaving 1.81 per cent. in the residue. If the compound $ZnFe_2O_4$ had been formed, 3.22 per cent. of zinc, instead of 1.81 per cent., ought to have remained insoluble. With the increase of iron in the mixture the quantity of zinc held back in the residue also grows. In experiments Numbers 4 and 5, all the zinc ought to have remained in the residue, but 39.42 and 39.65 per cent. was leached out. In experiment Number 6, in which zinc oxide was mixed with ferric oxide, practically all the zinc oxide was removed by ammonium sesquicarbonate, or no compound whatever was formed.

The tests, as far as they have been carried, tend to show that upon heating zinc oxide with ferrous sulphate various compounds of zinc and iron are formed, and not a single definite compound of the formula $ZnFe_2O_4$. The quantity of zinc remaining insoluble increases up to a certain point and then again decreases. Synthetical experiments with zinc oxide and ferrous sulphate cannot truly represent the process that takes place in roasting ferruginous blende; they can only point toward the direction of the reactions. The whole question of zinc ferrate must therefore be solved in a laboratory that is connected with central works treating blendic ores with different percentages of iron.

In dissolving the different samples of blende obtained in the sulphatizing-roasts, it was found that roasted Joplin blende dissolved readily in a mixture of potassium chlorate and nitric acid, but roasted Warren blende did not, but left behind a black residue, which was only slightly attacked by warm nitrohydrochloric acid, but dissolved readily when brought to a boiling heat.

BOOK REVIEWS.

Food Inspection and Analysis.[1]

In turning over these pages one hardly knows which feeling is uppermost, that of satisfaction that at last we have a book dealing with American conditions worthy to stand with the classic volumes of König and Blyth, or of keen regret that those who most need the information here given are prohibited by the price from consulting the scores of pages especially adapted to enlighten the consumer of household supplies.

The great advance in scientific knowledge in the past fifty years, as well as the change both in market conditions and in attitude of mind of dealer and purchaser, cannot be realized without a comparison of conditions as indicated in the three books — the one under review and Hassall's first book, issued in 1857, and the second, which was our authority, in 1875.

Today one is inclined to believe that some of the statements found in the earlier books were false. Certain it is that neither calves' brains nor chalk have ever been found in milk in the laboratories of the Institute, although in Hassall's second book, 1875, there is a plate showing the appearance of milk adulterated with sheep's brains.

In the first volumes of the "American Chemist," 1870 to 1875, the few references to adulteration of food were from foreign journals. Science was still to the average mind suggestive of cauldrons in dark caverns and necromancy in the factory. The sensational writer had credulous readers, and as late as 1880 the reviewer was appealed to by the family of a well-known business man who was giving up his esteemed breakfast of buckwheat cakes because of the newspaper story that ordinary syrup contained so much tin that the chemist could extract enough from a quart to hang in a ball around the neck of the bottle, and that the substance then newly put upon the market,

[1] Food Inspection and Analysis. For the Use of Public Analysts, Health Officers, Sanitary Chemists, and Food Economists. By Albert E. Leach, S.B., Analyst of the Massachusetts State Board of Health. New York: Wiley, 1904. 14 + 787 pp., ill., plates. $7.50.

glucose, contained so much free sulphuric acid as to eat out the lining of the stomach in a few weeks.

In the first general canvass made for the State Board of Health by the reviewer in 1879, it was found that in Massachusetts the staple articles of dry groceries were not then seriously affected. As the New York line was approached, cream of tartar and spices deteriorated. A fairly close watch upon the market has been kept by students in the laboratory since that time with the same result. It has become increasingly difficult to find examples corresponding to the book and newspaper accounts.

The great increase in canned and bottled goods has brought in a new element. Sixty-eight pages, nearly one-eleventh of the whole book under review, is given to these articles. One page of Hassall, 1875, dismisses "tinned vegetables."

The proportion of space given to the different articles indicates the importance of inspection, in other words, liability to adulteration or sophistication. Seventy-eight pages are given to milk; fifty-five to cereals, legumes, vegetables, and fruits; ninety-four to edible oils and fats. That is, the space is in proportion to the present need of investigation. In the 800 pages one can find nothing to leave out.

Especially to be commended is the full bibliography at the end of each section. The cuts and descriptions of apparatus will be of the greatest value to those fitting up new laboratories.

While from a scientific standpoint the book indicates a most satisfactory advance in results of investigation, it is to be especially commended for its sane and unbiased point of view. It is written by one who is neither an alarmist nor a controversialist. Any one may go to these pages with confidence that he is finding plain facts as far as they are known to the author.

If the public will only cease from following the traditions of the past and will sustain the efforts of state and city authorities so well illustrated in the volume before us, there will inevitably result a great increase of health and satisfaction in life.

E. H. R.

On the analytical side the author has covered in a very satisfactory manner the broad and constantly enlarging field of methods for food analysis. Further, it is clearly evident that the greater part of the procedures are given in the light of experience in the author's labora-

tory. They possess, therefore, a much greater value than would attend a mere compilation, however carefully made.

Among the points worthy of special commendation are the chapters on microscopical methods, together with the excellent reproductions of photomicrographs which accompany the text. The author is to be congratulated upon using these so freely rather than in placing reliance mainly on drawings. The experience of the reviewer leads to the belief that these examples of the actual appearance of the microscopic field will be of much greater aid to the novice than drawings, more or less idealized.

The tables of reagents and the definitions of food standards which accompany the methods will be found especially helpful.

The free use of references is a most praiseworthy feature.

There are naturally in a work of such comprehensive scope some omissions and some points on which there would be a difference of opinion. For instance, in the estimation of pentosans by phloroglucinol the use of Krober's factors should have been recommended rather than the older ones which are given. The question of the action of diastase upon hemicellulose is still an open one. These minor points, however, serve but to bring out more strongly the general excellence of the work. The book is one which every analytical chemist will be glad to have on his shelf for frequent reference, and to the active worker in food analysis it will be simply invaluable.

The publisher's work is fairly well done, but the press work is not always of the best. There are a number of typographical errors, and four of them on one page (255), some of them being omissions in important formulæ, do not show the careful proofreading that ought to characterize a work of this kind.

There is a very full index and the book is well bound.

A. G. W.

Sampling and Estimation of Ore.[1]

Under this title are collected all the papers on the above subject which appeared during the year 1903 in the *Engineering and Mining Journal*. The first seventy-five pages are devoted to the author's origi-

[1] The Sampling and Estimation of Ore in a Mine. By T. A. Rickard. New York Engineering and Mining Journal, 1904. 217 pp., ill., 8vo.

nal article. In his own words the problem is: "The determination of the amount of ore in the mine, the average value of it, and the cost of turning it into money." He attacks the subject both from the theoretical and the practical side, going into details as to tools, correct methods of procedure, and calculation of results; and illustrates by numerous examples from actual experience the necessity of a theoretical study of the conditions of each mine under examination.

The value of the original article is still further enhanced by the 124 pages of discussion which follow. In these contributions of twenty-five prominent mining engineers of experience, the author's ideas are discussed and enriched by a large amount of practical data. A noticeable feature is the almost entire freedom from controversy, which, unfortunately, does sometimes occur in a discussion of this kind.

The last nineteen pages are used by Mr. Rickard to sum up the additional data supplied by the discussion.

In reading this book it struck the writer that Mr. Rickard has, perhaps unconsciously, applied one of his principles of sampling to book writing. For just as he states that many small samples give better results in estimating a mine than one large one, so it would appear that the subject has been covered far better by the combined efforts of many men than it could have been by any single man, no matter how conversant with the subject he might be. Of the three divisions of the subject — amount of ore, value of it, and cost — the last is treated in much less detail than the first and second. This is natural since it is impossible to give any universal figures on costs. To go into this matter fully in all its phases would require a book in itself.

The net results of the work appear to be twofold. First, in describing the amount of ore more or less exposed in a mine it presents terms which shall be clear alike to the capitalist and to the mining man. Second, while it teaches that one can reach the goal of a successful mine examiner only by the path of experience, still it so marks out and smooths this path that the traveler cannot go far astray.

CHARLES E. LOCKE.

Experiments in General Chemistry.[1]

The authors have designed this series of experiments as a "guide for beginners" in chemistry, and it is easy to believe that they have found the course of instruction as laid down "productive of good." The experiments cover the common metals as well as the non-metals, and include the important methods of preparation and the characteristic reactions of the various elements as well as those of certain of their compounds. The questions which accompany the experiments are suggestive and helpful. An appendix contains various useful tables and the book is interleaved. The present edition has undergone revision, and it is stated that some experiments have been added since the last edition.

No attempt has been made apparently to introduce the ionic theory into this course of instruction, so far as one may judge from the questions. If the course is intended for young pupils, in secondary schools, this is, perhaps, a wise proceeding; if students of college age are to be instructed, many will find ground for criticism in this omission. On the other hand, some will question whether the "beginner" can properly undertake to carry out a vapor density determination by the Victor Meyer method understandingly within a few exercises of the opening of his course; or again, whether it is wise to give the pupil the impression that he has actually "verified" the principle of the conservation of mass by a necessarily crude quantitative experiment. But an experiment book is, after all, only the skeleton of the real body of the instruction, of which the flesh, blood, and vitality must come from the instructor himself. When these factors are what they should be such criticism as is implied above may hit wide of the mark. It is undoubtedly true that there is much to interest the thoughtful teacher in this little volume.

H. P. Talbot.

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[1] Experiments Arranged for Students in General Chemistry. By Edgar F. Smith and Harry F. Keller. Edition 5. Philadelphia: P. Blakiston's Son & Co., 1904. 4 + 94 pp., 40 ill.

Foundry Chemistry.[1]

In endeavoring to put foundry work on a scientific basis, to control the properties of various irons by means of analysis, and to overcome the prejudiced rule of thumb methods of the average foundryman, the author deserves credit. In offering for the use of a class of people not scientifically trained a book on the analysis of foundry materials, it is necessary to make the statements in the book more or less arbitrary and dogmatic, and on this account the book cannot be subjected to the usual methods of criticism. If the book is successful in teaching any foundryman the extreme value of chemical analysis in regulating and controlling his products, we should be thankful and then hope that he may be given his chemistry in a less arbitrary and more scientific manner in the future. The foundryman may, however, have some idea of the significance of figures, and may question the use of a factor carried out to the eleventh decimal for the conversion of the iron value of a potassium permanganate solution into the phosphorus value.

The book is divided into two parts, the first dealing with the taking of samples and the analysis for the various constituents of the ores, coals, cokes, and the different grades of iron; the second part is a discussion of the different grades of iron and the influence of the elements in affecting their properties.

H. F.

Transactions of the American Institute of Electrical Engineers.[2]

It seems to be an established custom now for the "Transactions of the American Institute of Electrical Engineers" to be divided into two volumes each year. We have before us Volume XX, which covers the meetings held from June to December, 1902, and Volume XXI, which continues the record to June, 1903. Both volumes in their completed form were published, however, in 1904, Volume XX having appeared in July, and Volume XXI in October.

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[1] Methods of Chemical Analysis and Foundry Chemistry. By Frank L. Crobaugh, M.S., Professor of Chemistry, Cleveland Homeopathic Medical College, Cleveland. Second edition. Published by the author. 109 pp. Price, $2.00.

[2] Transactions American Institute of Electrical Engineers, Volume XX, July to December, 1902. New York, 1904. 415 pp., ill., 8vo. Same, Volume XXI, January to June, 1903. New York, 1904. 610 pp., ill.

As in previous volumes, so in these the transactions of each meeting are devoted to a single subject, on which there may be one or several principal papers, followed by a general discussion, all of which is printed in full. Thus we find discussed in Volume XX the application of alternating currents to electric railways, a series of papers on photometry and illumination, the control of motors at variable speed, breaking and traction breaks. The subjects dealt with in Volume XXI are telephony, the lighting of railway trains, lines for the transmission of high-tension currents, radio-active substances, tendencies in the development of central stations, machines for the generation and use of alternating currents, the theory of alternating currents. Many of the articles are illustrated with cuts made from photographs, plans, or diagrams.

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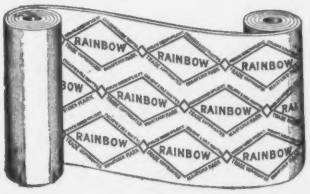

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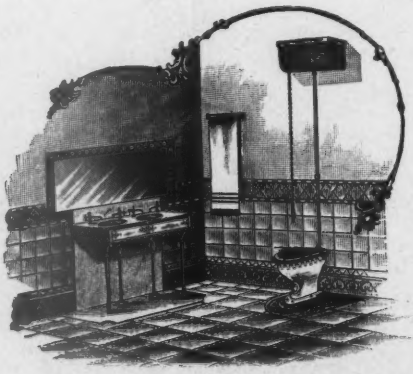

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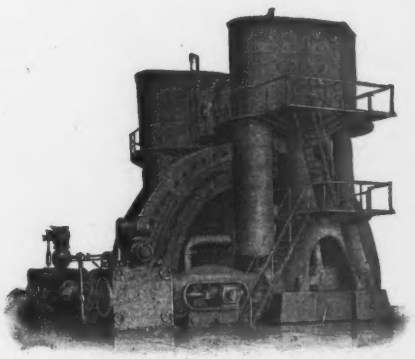

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